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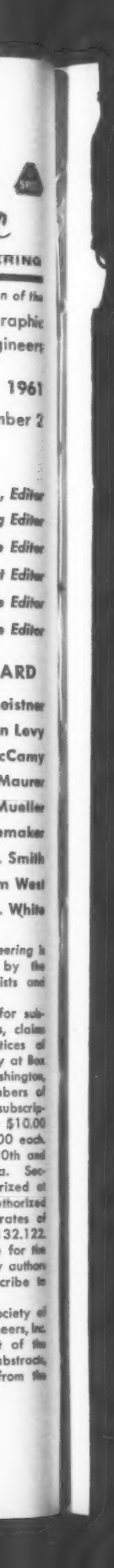


PHOTOGRAPHIC SCIENCE AND ENGINEERING
Volume 5, Number 2, March-April 1961

Our Present Understanding of Spectral Sensitization

B. H. CARROLL, *Research Laboratories, Eastman Kodak Company, Rochester, N.Y.*

This paper is a critical review of the literature of spectral sensitization including unpublished material presented at the Colloque International de Photographie Scientifique at Liège in 1959. There is good agreement that (1) spectral sensitization occurs by a primary process in which the excitation energy of the adsorbed dye is used to raise an electron to the conduction band of the silver halide; the secondary processes are then the same as when the energy is absorbed by the silver halide. However, rates and efficiencies of secondary processes in an emulsion may be modified by changes in environment; the presence of the sensitizing dye may be such a change. (2) Surface states in the silver halide take part in the process of latent-image formation by quanta smaller than those absorbed by the silver halide itself. There is no experimental evidence which proves whether the primary process occurs by transfer of energy or an electron from the dye molecule, and the question appears somewhat academic. It is suggested that desensitization can be explained by the ability of dyes to trap holes and facilitate their recombination with electrons.

This paper is an attempt to summarize the experimental facts on spectral sensitization of silver halide emulsions, and the principal interpretations of these facts. It may best be introduced by a description of the system to be considered, in terms of its chemical composition and physical properties.

Adsorption of Dyes

A spectrally sensitized emulsion is a dispersion of silver halide crystals in a water-permeable colloid, which has a suitable dye or dyes adsorbed to the crystals ("grains"). The adsorption is a necessary condition for sensitization.[1*] In liquid emulsion, the adsorption isotherm usually shows a saturation level corresponding to a monomolecular layer of dye close packed in edge-on orientation,[2,3] when the solubility of the dye in water makes it possible to follow the isotherm to this point; however, saturation may occur at less than complete coverage[3,4] (Fig. 1). Many dyes are so insoluble that their adsorption is irreversible at working levels, and the adsorption of other dyes may be effectively irreversible in the absence of competing materials such as gelatin. However, when the solubility of the dye is adequate, the adsorption is reversible. Adsorption of dye has been shown to be in equilibrium with adsorption of gelatin;[3,5] normally this equilibrium lies at nearly complete adsorption of the dye. It should also be remembered that there may be appreciable changes on drying the emulsion; these are difficult to follow, but changes in spectral absorption indicate that, for example, the weakly adsorbed dye erythrosin is more completely adsorbed in the dried coating than in the liquid emulsion.

There is frequently a discontinuity in the "toe" of the adsorption isotherm, which is associated with the beginning of oriented close-packed adsorption and corresponding molecular interaction; this has been correlated with a change in spectral absorption and an increase in heat of adsorption in the few cases tested.[3] However, as in many other systems, the net heat of adsorption calculated from the temperature coefficient is higher for the first portions of dye adsorbed than for the rest; this is a strong indication that there are portions of the grain surface where the adsorption forces are stronger than the average. Within these limitations, the adsorption isotherms of most sensitizing dyes are fitted quite accurately by the Langmuir equation, $m/M = kc/(1 + bc)$. A few dyes have been found to follow the Freundlich equation, $m^n = kc$, with no saturation level.† A saturation plateau may be followed by multilayer adsorption at higher concentrations, but this region is of little interest since the optimum concentration for sensitization appears always to be less than complete coverage. The constants in the equation vary considerably, as might be expected, with the solubility of the dye in water;[3,4,6] this is probably one of the factors which lead to increasing adsorption of the dyes in a series with increasing chain length.[4]

The presence of anions which reduce the dye solubility tends to increase adsorption,[6] and dye

Received 21 November 1960. This paper is a revision of a talk given at the Colloque International de Photographie Scientifique, Liège, 14-19 September 1959. In accordance with discussion of nomenclature at the conference, the term "spectral sensitization" will be used in place of the less definite "optical sensitization." No attempt has been made to include a historically complete bibliography or to indicate priority of discoveries; preference has been given to recent papers which summarize information.

* References are listed at the end of the paper.

† The Langmuir and the Freundlich equations have been written in the same symbols:
c is the concentration of free dye in equilibrium with the dyed grains;
m is the amount of dye adsorbed per unit mass of silver halide;
k, n, and b are constants;
M is the value of m at the saturation level.

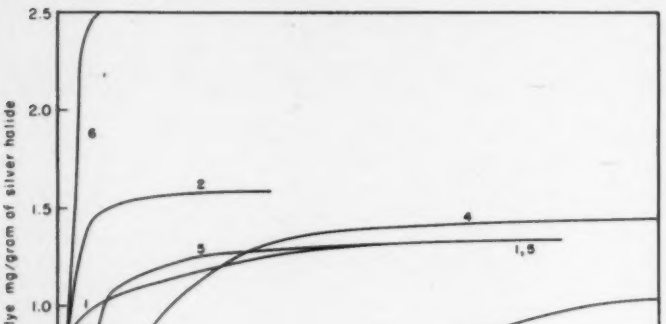


Fig. 1. Figure 166 from *The Theory of the Photographic Process* (rev. ed.), by C. E. K. Mees (Macmillan, New York, 1954). Adsorption of some cyanine dyes in emulsion at 40°C. (1) 1,1′-diethyl-2,2′-cyanine iodide; (2) 3,3′-diethylthiacarbocyanine iodide; (3) 1,1′,3,3′-tetramethyl-2,2′-cyanine iodide; (4) 3,3′-diethyloxacarbocyanine iodide; (5) 3,3′-dimethyloxacarbocyanine iodide; (6) 9-ethyl-3,3′-dimethyloxacarbocyanine iodide.

solvents, such as color couplers, may interfere seriously with adsorption.[7] Heats of adsorption varied by nearly 3:1 among dyes tested in the same emulsion. As similar isotherms are found for cyanines, for merocyanines with no specific affinity for ions of the silver halide lattice, and for merocyanines containing groups such as >C=S which should be attracted to silver ions, it is a reasonable inference that van der Waals' forces are more important in dye adsorption than electrostatic forces. It should be noted that the distinction between acid and basic dyes, important in textile dyeing, has no direct significance in adsorption to silver halides or in sensitization. The edge-on arrangement of dye molecules has been found in basic, neutral, and acid dyes. There is no reason to believe that it is essential to sensitization. Probably the first molecules of all dyes are adsorbed flat on the surface, and the edge-on position is assumed when more of the surface is covered; some dyes may remain flat. The presence of very firmly adsorbed compounds, such as thioureas, may interfere with dye adsorption.[8] When electrostatic forces are in opposition to adsorption, as in adsorption of basic dyes to silver halide in the presence of excess silver ions, there may be marked reduction in adsorption.[3]

Structure of Sensitizing Dyes

Spectral sensitization has been produced by many classes of dyes, but those in use are predominantly polymethine dyes having the amidinium and amide types of resonance (Fig. 2). Dyes having the oxonol type of resonance may sensitize, and one of them, erythrosin, was of major importance in early orthochromatic plates, but these are much less common. Published information on the relations between structure and photographic sensitizing properties of dyes does not provide material for a satisfactory discussion of this subject as a whole. The extensive patent literature[9] provides data on the relations between structure and spectral region of sensitization, and there are several, more quantitative studies[7,10–16] of dyes of single classes, some of them based on data for many dyes. The relations between a single photographic property and structural changes in a single dye class seem to represent the present limits of success in this field. Furthermore, it should be emphasized that the effectiveness of spectral sensitization by a given dye depends on such emulsion variables as the composition of the silver halide, the silver- and hydrogen-ion concentrations,[17] and the presence of other compounds,[18] so that the photographic characteristics of a dye are not defined by any single test.

Absorption Spectrum of Dyes in Solution

The relations between the structures and spectral absorptions of polymethine dyes in molecular solu-

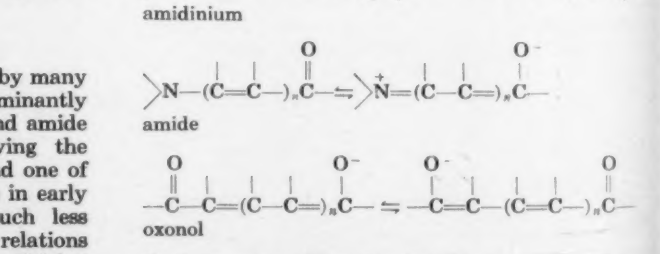


Fig. 2. Resonance systems of sensitizing dyes.

tion have been studied at length. Their wide range of structures and spectral absorptions, and their sharp absorption bands, have made the sensitizing dyes outstandingly useful in the field of "color and constitution." Precise relations have been derived connecting spectral absorption maxima in molecular solution with chain length, basicity and acidity of nuclei, and polarity of solvent.[19] In very dilute aqueous solutions (about 10^{-6}M) the spectral absorption of dyes is similar to that in organic solvents, but at higher concentrations there are almost always major changes resulting from molecular interaction and aggregation.[20,21] The presence of gelatin in the solution may introduce further modification.[22]

The aqueous solutions of polymethine dyes usually have distinct new absorption bands which may replace the "molecular" band as concentration is increased. Bands at shorter wavelengths, with bandwidths of the same order as the molecular band, are the most common, and it is possible to have more than one per dye; for brevity, these will be called H-bands. This type of band is known in solutions of other types of dyes,[23] and the change in relative strength of the "molecular" band and H-band has been found in several cases[20,23] to fit equations derived from the assumption of a mass-law equilibrium between a monomeric form of the dye responsible for the molecular band and a low polymer or series of polymers for the H-band.

Another type of band, called for brevity J-bands, always lies at longer wavelengths than the molecular band of the dye and is characterized by absorption coefficients as much as twice those of the molecular band, and by small bandwidths. J-bands are also concentration dependent, and the equilibrium may follow mass-law equations,[20c,d] but the appearance of these bands has been found to correlate with the presence of definite structural arrangements of dye molecules in the solutions.[24] It seems justifiable to assume that the band comes from a specific ordered array of dye molecules, which is apparently independent of the number of molecules in the array once the necessary minimum number has been established; this minimum may be as low as three.[25] The form of the array found in solution has been threads in which the molecules are parallel to each other, normal or sometimes inclined to the length of the thread, and this structure has been found to persist in dried films of dye on glass or mica. The spacing determined by x-ray diffraction corresponds to the thickness of the heterocyclic rings in the dyes.[24] This type of spectral absorption is a most interesting and widely investigated subject in itself, and there has been a natural tendency to give it a more fundamental role in spectral sensitization than is warranted.

Spectral Absorption and Structure of Adsorbed Dye Layers

The spectral absorption of a dyed emulsion is dependent on the optical properties of the emulsion, as well as on the absorption of the dye as modified by this environment. Unless the emulsion is very fine grained or very thinly coated, scattering of light within an emulsion layer increases the path of light by a factor of two or more and thus increases the absorption by both dye and silver halide. No complete solution has been reached for the mathematical expression of absorption under these conditions,[26] but determination of total spectral transmittance and reflectance gives adequate data for most purposes, including comparison of the absorption of dyes in solution and in emulsion.

In the emulsion, the dye is adsorbed to the surface of silver halide, an ionic lattice of high polarity and high refractive index. The absorption bands of dyes in low concentrations, where they appear to act as individual molecules, are broadened and displaced toward longer wavelengths than the bands in the dilute solutions of the same dyes; the displacement is in accordance with the increase in refractive index. Under these conditions, the displacement of the maxima of cyanine dyes is usually 20–40 mμ, while that of merocyanines may vary widely with structure, indicating that the change in refractive index is not the only factor.[14] It has been suggested that energy of adsorption is a factor in sensitization. However, adsorption of dyes on photochemically inert substrates produces similar displacements, and some of the changes may be produced by adding salts to aqueous dye solutions, so that it does not seem probable that the energy of adsorption contributes directly to sensitization.[27] The dye in the emulsion has been adsorbed from an aqueous solution containing gelatin, and it has been suggested[28] that aggregates of dye formed in solution might be adsorbed as such, but grains having dye aggregates on the surface are often in equilibrium with dye in molecular solution.[3] Most cyanine and merocyanine dyes in the emulsion have absorption maxima corresponding to H-bands in their aqueous solutions;[29] the displacement of the maxima of H-bands from solution to emulsion is less, on the average, than that of molecular bands. While the molecular band of the dye appears at the lowest concentrations in emulsion, and the H-band becomes more prominent as concentration is increased, no simple relation between the band strengths and concentration can be given.

In some cases, dyes have a J-band both in solution and in emulsion, and when this occurs the maxima are at the same wavelength; apparently the spectral absorption is determined by the interaction between molecules in this specific array, and the influence of external factors such as adsorption is slight. It is significant that, while some dyes readily form the J-band both in solution and on emulsion grains, others form it with much more difficulty in one condition or the other. This suggests that the band depends on a particular orientation of the molecules which may be aided or hindered by adsorption to the silver halide lattice. Sharp bands at long wavelengths, not necessarily identical with the

J-bands, have been found in crystals of dyes and in films of dyes on glass or mica surfaces. The edge-on arrangement of adsorbed dye molecules is normal, whether or not "aggregation" to give J-bands occurs, and no certain difference in spacing of molecules in the layer has been found to be associated with J-band formation;[3] however, x-ray diffraction measurements on layers of 1,1′-diethyl-2,2′-cyanine on mica indicated a spacing corresponding to overlapping of dye molecules lying at an angle of about 35° from normal.[24a]

J-band formation in emulsion is concentration dependent, but in a peculiar fashion; the photographic evidence indicates that, as concentration is increased, the characteristic absorption appears on an increasing proportion of the emulsion grains[30] since D_{max} and γ for exposures to the wavelength of the J-band increase from low values to normal for the emulsion. The J-band represents a state of minimum potential energy, since it is favored by digestion of the emulsion with the dye[31] and is associated with increased heat of adsorption.[3,5] With increasing concentration, the J-band may dominate the absorption of the dye, with marked reduction in the strength of H-bands as well as molecular absorption.[29] However, it appears probable that the arrangement of dyes in this form on emulsion grains is never complete, since dye adsorbed to a sheet crystal of high perfection has been found to form a J-band even more selective than in emulsion.[32] The dye layer may contain other molecules which possibly help to maintain the structure; the presence of water is essential in some cases,[27] and patents[33] give numerous examples of organic compounds which favor J-band formation and presumably play a part like water. Closely related dyes may form mixed aggregates, with maxima intermediate between those of the individual dyes.[30c,d]

J-band formation is clearly favored by certain types of dye structure: 2′-cyanines; thia-, selena- and 5-phenyloxacarbocyanines with substitution in the central position of the chain; and carbocyanines in which the chain is part of a ring system may be cited as well-known examples. It is much less common in merocyanine dyes, and unreported in such types as hemicyanines and styryls; merocarbocyanines derived from indolenine and pyrazolone[2] and those derived from malononitrile[34] are conspicuous examples of merocyanines forming J-bands. Brooker[35] has pointed out that the cyanines giving J-bands have the common characteristic of a "compact" or "rigid"[36] structure which is planar but has minimum space for change of band angles; Anderson's observation[34] that the merocyanines from malononitrile have a minimum number of stereoisomers is related to this, since a rigid structure usually is more restricted in number of stereoisomers. However, it is evident that there are other variables: the indolenine-pyrazolone merocarbocyanines are conspicuous cases of aggregating dyes which do not conform to the rule stated.

Relative Efficiency of Spectral Sensitization

The maximum of sensitivity of an emulsion normally corresponds to the maximum of spectral absorption;[27] because the spectral absorption may be built up from overlapping bands in which the dye may have varying effectiveness, sensitivity in the region of spectral sensitization is not always proportional to absorption. The most generally useful expression for the effectiveness of sensitization is the relative quantum yield (φ_r)[37]—measured by the number of quanta absorbed by the silver halide of an emulsion to produce a given developed density, divided by the number of quanta in the region of spectral sensitization which must be absorbed to give the same density. The energy absorbed in the emulsion layer may be calculated as (1 − total reflectance − total transmittance). With the best sensitizations, φ_r reaches a value of 1.0. It appears to be characteristic of the dye–emulsion system, since, unless there are changes in aggregation, it is independent of dye concentration, of the wavelength chosen for measurement within an absorption band, and of the emulsion coating thickness, within the limits of precision of measurement, which are rather wide for low dye concentrations. A characteristic value may be obtained for a dye–emulsion system whether it is 1.0 or a much smaller fraction. The maximum value of 1.0 is to be anticipated from all theories of sensitization which assume that the primary process is the liberation of an electron for each quantum absorbed.

It should be remembered that emulsions with a range of relative and absolute spectral sensitivities may have the same value of φ_r. The relations actually observed are dependent on the experimental fact that the optimum dye concentration for a given dye corresponds to a roughly constant coverage of the silver halide surface by the dye. Therefore, the finer the emulsion grains, the more dye can be used, and the higher the absorption of, for example, red, for a given amount of emulsion per unit area of film. In absolute terms, the absorption of red will be greater in the finer-grained emulsions. It will also be greater in relation to the absorption of violet by the silver halide since, over the usual range of grain sizes, the absorption by the silver halide is nearly independent of grain size, being a volume absorption; it falls off only in emulsions so fine-grained as to have little scatter. It has recently been reported[38] by Zwicky that in a series of similar emulsions with varying grain size, the sensitivity in the violet varied approximately as the cube of the grain diameter, and sensitivity in the green varied as the square. As the figures for dye concentration and grain size show that the dye per unit surface was constant to ±15%, these relations indicate that sensitivity was proportional to the absorption per grain in the region of absorption of both the silver halide and the dye; this relation of the sensitivity to surface is dependent on the use of dye at concentrations which cover a constant fraction of the surface.

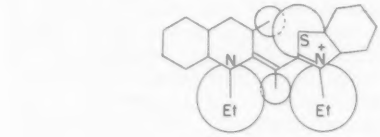
The ratio of absorption and sensitivity in the region of spectral sensitization to that in the violet, for a given specific surface of silver halide, depends on the composition of the silver halide, since the integrated absorption of white light by (undyed) silver bromoiodide is of the order of ten times that of silver chloride. The increase in white-light speed of the emulsion produced by spectral sensitization with dye having a given φ_r, accordingly, is greater for fine-grained emulsions, and for silver chloride and chlorobromide, than for the relatively coarse-grained bromoiodide emulsions used for negative films. Finally, the absolute sensitivity of a spectrally sensitized emulsion depends on the inherent sensitivity of the emulsion; if, for example, two portions of grains from the same emulsion precipitation, one portion with and the other without chemical sensitization, are spectrally sensitized with the same amount of dye, the ratio of sensitivity in the red and blue will be the same.[39a,b] A further distinction should be made here. Although chemical sensitization increases sensitivity equally in all spectral regions to which an emulsion is sensitive, this does not mean that a dye may not interact with chemical sensitization; for example, a dye may have different effects on blue speed of the same emulsion with primitive, reduction-, and sulfur-sensitizations.[39c]

Desensitization by Sensitizing Dyes

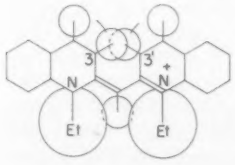
The influence of the dye on the emulsion is not confined to exposures in the region of dye absorption. One of the effects, desensitization, must be considered in any comparison of the properties of dyes. It should be remembered that, even in the most intense exposures, only a minute fraction of the dye molecules are excited at a time, and it is not surprising that the tightly adsorbed dye molecules in the ground state should influence the sensitivity of the emulsion. Desensitization by sensitizing dyes may be measured by the change in sensitivity of the emulsion to spectral regions in which the dyes do not absorb.[37,40–46] It is the primary factor limiting the amount of dye which can profitably be used. The calculation of φ_r by the method just outlined implies that desensitization by the dye in the ground state equally affects exposures in any spectral region. No direct test for this assumption has been devised, but the self-consistency of the results obtained with it carry considerable weight; the probability that φ_r should remain constant over a series of concentrations, in many dye–emulsion combinations, is very small on any other hypothesis. As will be shown later, it is consistent with most proposed mechanisms of sensitization. As might be anticipated, the desensitization in a given dye–emulsion combination is dependent on intensity of illumination. In any given emulsion, the reciprocity-law failure plotted on a time scale is independent of the wavelength of exposure,[47] but the addition of dye to the emulsion may have changed the reciprocity characteristics for all wavelengths.[48]

Relation of Dye Structure to Sensitization and Desensitization

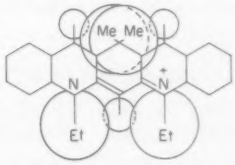
The relations of dye structures to relative quantum yield and to desensitization are more easily discussed together than separately. Quantum yield may vary within the region of spectral absorption by a single dye, since it frequently is lower for an H-band or J-band than for the molecular absorption, but it often is practically constant. The well-known tendency of cyanines carrying methyl groups on the heterocyclic nitrogens to be inferior to the corresponding N-ethyl dyes has been correlated with H-band formation[15] and consequent inefficiency. Absorption in the J-band region is frequently, but not necessarily, accompanied by a lower value of φ_r. When φ_r for a J-band approaches unity, sensitization is strong because of the intense absorption. The relations of structure to over-all strength of sensitization have been discussed in many papers (for example, References 7, 10–16, 35, 49, and 50), but such regularities as have been observed are limited in scope and not adapted to summary. There is one valid generalization of a negative character—that if the structure of a dye is such that the resonating chain cannot lie in a plane, the dye by itself will not sensitize.[35] This rule is illustrated by three well-known dyes in Fig. 3.



1,3 diethyl thia 2' cyanine



1,1'diethyl 2,2' cyanine



1,1' diethyl 3,3' dimethyl 2,2' cyanine

Fig. 3. Structural formulas of planar and nonplanar dyes.

Structural formulas have been drawn according to the available data for atomic radii, bond lengths, and bond angles, for planar arrangements of the atoms. The first dye, 1′,3-diethylthia-2′-cyanine, has no overlap of groups and is an efficient sensitizer. The second, 1,1′-diethyl-2,2′-cyanine, has an overlap of the hydrogen atoms in the 3- and 3′-positions, which could be removed by moderate bending of the bonds between the nuclei; by itself, this dye has a relative quantum yield which is about one-tenth. The third, 1,1′-diethyl-3,3′-dimethyl-2,2′-cyanine, has an overlap of the methyl groups in the 3- and 3′-positions so great that it can be removed only by twisting the nuclei out of planarity; its quantum yield, when used alone, is too low to measure.

The published information on the relation of structure to desensitization is as extensive as on sensitization; unfortunately, much of it is based on the assumption that a given dye is a sensitizer or a desensitizer. The fact that spectral sensitization and desensitization can be properties of the same dye has been understood more or less specifically by those interested in the subject for some time,[37,40-46] but has not become widely known until recently. Relatively small changes in structure of typical sensitizing dyes such as cyanines can so increase their desensitizing action that they have no practical value as sensitizers. Introduction of strongly negative groups, such as nitro, is one such change; desensitization by polymethine dyes with such modifications is powerful because of the strong adsorption of the dyes and their capacity for interaction with silver halide. Substitution of a nitrogen for a =CH— group of the resonating chain is another change capable of producing strong desensitizers; it was first observed by Kendall[51] that this occurs when the nitrogen atom in the chain is separated from those at the ends by an even number of carbon atoms.

The chemistry of the typical desensitizers has been summarized by Schuloff[52] and Brooker.[53] Desensitization may be correlated with the structure of dyes, but not explained by their chemical properties, whether the dyes are desensitizers only or spectral sensitizers. Among dyes which can be classed as strong spectral sensitizers, there are major differences in desensitization which may be illustrated by those between cyanines derived from benzothiazole and from 4-phenylthiazole.[37] It is somewhat surprising that desensitizing and relative quantum yield of a dye appear to be independent characteristics; a dye may combine strong desensitization with either low or high φ_r.[37]

Surface Actions of Dyes

The presence of sensitizing dyes on the silver halide surface obviously may affect reactivity. Lüppo-Cramer[54] observed the acceleration of hydroquinone development by basic dyes, and retardation of development under some other conditions. Fog induced by sensitizing dyes is well known,[54] and while some of the reports in the earlier literature may reflect only the purity of the available dyes, fog is characteristic of some cyanines, as well as of dyes like methylene blue. Less well known is the stabilization of the emulsion against further chemical sensitization and fog,[55] presumably by covering reactive areas.

Although absorption of light by the dye is confined to the surface of the grain, and its influence on such properties as developability is directly connected with its presence on the surface, latent image resulting from exposure to light absorbed by the dye has practically the same distribution between surface and internal image as that from light absorbed by the silver halide.[56] This result in emulsion s in accordance with experiments in sheet crystals showing that radiation absorbed only at the surface may produce image many microns below; exposures by ultraviolet radiation, which is absorbed in the first micron of silver bromide, and by light absorbed only by dye on the surface are alike in this respect.[57]

Spectral sensitization of the print-out process can be produced by the major types of sensitizing dyes, and the results applied, with the usual reservations for any such extrapolation, to latent-image formation. In aqueous sols of silver halide containing halogen acceptors, the quantum yield approaches one in the region of spectral sensitization as well as in the violet.[58] On dry gelatin emulsions without acceptors, the print-out process is inefficient in the violet, and extremely inefficient in the region of spectral sensitization. The rapid bleaching of the dyes which occurs on heavy exposures of dry emulsions, either to blue light or to light absorbed by the dye, indicates that most of the positive holes formed in the primary process are liberated as halogen. This may not be true in the latent-image range of exposure if silver sulfide acts as a halogen acceptor; the failure of halogen acceptors to increase sensitivity for latent-image formation under normal exposure conditions is good evidence that the halogen is somehow eliminated. There is evidence that a single dye molecule may act repeatedly in photolysis,[59] indicating that, if it takes part in the reaction, it is promptly regenerated. However, dyes may promote solarization on overexposure,[60] presumably acting as halogen carriers in accordance with their known capacity for reversible acceptance of bromine.[58]

Photoconductivity

One of the major difficulties in photographic research is the scarcity of independent measurements of the process of latent-image formation. One measurement which is available in the study of spectral sensitization is photoconductivity. Some semiconductors, such as silver and thallous halides, zinc oxide, and cadmium sulfide, show photoconductivity which may be sensitized by dyes to spectral regions which the substrate does not absorb.[61,62] The sensitized photoconductivity of silver halides can be measured in conventional gelatin emulsions;[63,64] it is essentially inertia free and can reasonably be considered a measure of the primary photoprocess. The use of emulsion instead of sheet crystals provides strong absorption in the region of sensitization and the results are directly applicable.

The spectral sensitivity of the emulsion for photoconductivity is parallel to that for latent-image formation; changes in relative quantum yield produce proportional changes in these quantities. The same dyes adsorbed on insensitive crystals, such as lead bromide, produce no photoconductivity, so that under the conditions of the emulsion, the photoconductivity appears to be sensitization of the silver halides, and not conductivity of the dye layer. On zinc oxide,[61] typical photographic sensitizers gave spectral sensitization of photoconductivity,

while typical desensitizers did not; however, some of these desensitizers sensitized thallous iodide. One of the most significant observations is that desensitization by dyes does not reduce photoconductivity of silver halide emulsions in the blue and violet; desensitization, therefore, occurs in the secondary processes of latent-image formation and does not represent an interference with the primary process.

Photoconductivity of layers of pure dyes has been observed by many experimenters, but results have been difficult to reproduce, and the conductivity observed until recently was some orders of magnitude lower than that of the same dyes adsorbed to semiconductors such as silver halides or zinc oxide. However, recent work by Meier and Noddack,[65] using thin films deposited on grid electrodes of rhodium on glass, has indicated that some sensitizing dyes are photoconductors with the ratio of (electrons liberated)/(quanta absorbed) approaching one.

Effects of Environment on Sensitization

Evidence on mechanism of sensitization is also provided by the interaction of sensitization with the emulsion environment, for example, temperature, composition of silver halide, silver-ion concentration, and the presence of other dyes or compounds.

Sensitivity in the region of spectral sensitization has a larger temperature coefficient than in the violet; Evans's data[66] show that between room temperature and −186°C, the decrease was 10–100 × greater in the region of spectral sensitization, and there were indications that the weaker sensitizations had larger temperature coefficients. No systematic increase of temperature coefficient with increasing wavelength was evident. The absorption of silver halide generally decreased more than that of the dye over this range,[67] so the decrease in sensitization was caused by loss of transfer efficiency, not absorption.

The composition of the emulsion in terms of silver halide is less critical than might be expected, since silver chloride, bromide, bromoiodide, and even pure iodide may be sensitized over a wide spectral range by the same types of dyes;[68] the differences in the long-wavelength absorption limits of these halides do not reflect any basic difference in capacity for sensitizing, although there may be, of course, quantitative variations in efficiency of sensitization of chloride, bromide, bromoiodide, and iodide. Silver halides may be sensitized only for the regions which they do not strongly absorb, so that silver chloride may be sensitized for the violet, while silver bromoiodide may not be. Differences of this type, and the differences in the effect of spectral sensitizing on the white-light speed of an emulsion described in the section on *Relative Efficiency of Spectral Sensitization*, above, are easily confused with differences in efficiency of sensitization. Some dyes have been reported to develop J-bands more readily with increasing iodide in bromoiodide emulsions;[69] effects of this type obviously may be of practical importance, but do not indicate basic differences in sensitization.

The effect of relative silver- and halide-ion concentrations in the emulsion on the sensitivity is generally larger in spectrally sensitized emulsions than unsensitized. The importance of this factor depends on the dye,[70] being large for many infrared sensitizers; both relative quantum yield and desensitization may be favorably affected by increased silver-ion concentration. Such an increase in silver-ion concentration is the most important effect of after-treatment by bathing, commonly called hypersensitization.[71] The silver-ion concentration after bathing and drying increases with composition of the bath in the order: water, amines, ammonia, and ammonia plus dissolved silver salts; hypersensitization is essentially a means of securing, by low-temperature treatment in which the emulsion is wet only for a brief period, silver-ion concentrations which would cause instability in warm liquid emulsion. Sensitivity for low intensities is increased more than for high.

The mutual effects of two sensitizing dyes, or a dye and a colorless compound, in an emulsion are generally complicated, but some of them may be interpreted to give important evidence on the mechanism of sensitization. The mutual effect of two dyes is, much more often than not, unfavorable. For example, if activation energy may be interchanged between two dyes more readily than between either dye and the silver halide, the relative quantum yield of the mixture should approach that of the less efficient component. This is clearly demonstrated in mixtures of planar and nonplanar dyes of similar structure.[72] The presence of one molecule of nonplanar dye per hundred of planar materially reduces the relative quantum yield, provided the absorptions of the dyes overlap. As would be predicted, such effects occur only when the nonplanar dye may be activated by a quantum absorbed by the planar dye; if the nonplanar dye absorbs at shorter wavelengths, the antisensitization does not occur except when the energy differences are so small that they may be made up by thermal activation.

This wavelength relation was tested using three nonplanar dyes, each of which was coated with a series of related sensitizers so that the absorption of the sensitizer varied from shorter to longer than that of the antisensitizer; when the λ_{max} of the sensitizer was longer than that of the antisensitizer by 50–60 mμ or more, the antisensitization stopped. Antisensitization was evident in photoconductivity of emulsions as well as in photographic experiments.[63]

The converse effect, known as supersensitization, occurs in a small fraction of dye combinations. Its existence is established when addition of a colorless compound, or of a second dye sensitizing for a different region, increases sensitization by a given dye, and it is easily distinguishable from chemical sensitization when the increase in the region of spectral sensitization is larger than in the violet. It is more difficult to define when both dyes sensitize for the same region, but its existence is established

when, at any wavelength whatever, the combination of dyes gives more sensitivity than the maximum obtainable at that wavelength by either of the dyes alone. Supersensitization may take at least three forms. The second dye or compound may (1) increase the relative quantum yield of the first dye, (2) make favorable changes in spectral absorption, for example, increasing the strength of a J-band, (3) reduce desensitization by the dye. Case (3) can be distinguished from chemical sensitization because speed in the violet does not exceed that of the unsensitized emulsion.

The relations between structures of sensitizer and supersensitizer are of little help in interpretation of mechanism; the useful combinations cover a wide range of compounds and dye types;[73] and the effects are highly specific. It may be said that no cases are reported in which the supersensitizing compound is very closely related to the dye supersensitized, e.g., a homologue. All supersensitizers which increase relative quantum yields have conjugated chains of carbon atoms.[72,74,75] It should be emphasized that they are not themselves likely to be better sensitizers than the dye supersensitized; however, there are probably no cases where quantum yield is increased by a compound which is itself lacking in strong selective spectral absorption.

The supersensitizer apparently becomes a part of the dye layer; its own maximum often is absent from the spectral absorption of the combination.[72] On increasing the concentration of the supersensitizer[74,76] past a critical ratio in a mixture with a dye having a J-band, the J-band is replaced by the molecular band of the dye; for 1,1′-diethyl-2,2′-cyanine, this occurs in the vicinity of 1 molecule of supersensitizer to 3 of the 2,2′-cyanine. This may be taken as an indication that the unit for the characteristic J-band absorption is about 3 molecules, in agreement with mass-law data for polymerization of the dye.[25] However, both the apparent absorption of a compound into the dye layer and the destruction of the J-band may be observed[76] where there is no supersensitization.

There is no critical relation between spectral absorption of the dye supersensitized and the supersensitizer. The maximum of the supersensitizer may be either at shorter or longer wavelength, and separated from the maximum of the sensitizer widely enough so that overlap of bands is at least very slight. In a series of related supersensitizing compounds,[74] failure to supersensitize occurred when the maximum absorption of the supersensitizer was too far short of that of the dye supersensitized; but the specific variations in supersensitization with structure are so great that it is difficult to be sure of the significance of this result.

The photoconductivity of emulsions containing supersensitizing combinations of dyes has been found to be increased, relative to that of the first dye alone, in proportion to the increase in relative quantum yield.[63] Supersensitizers have been found to be efficient quenchers of the fluorescence of dyes which they supersensitize.[72]

The possible degree of supersensitization of a given dye obviously depends on its inherent relative quantum yield, absorption, and desensitization. It is, however, surprising that the possibility of supersensitization extends to nonplanar dyes in which the quantum yield is so low that sensitization cannot be detected. This has been demonstrated[72] with nonplanar 2′-cyanines, using supersensitizers which are highly effective for planar 2′-cyanines; φ, reached a value of about 0.5, compared to <0.001 for the nonplanar dye alone. The inefficiency of the nonplanar dyes seems most likely to be caused by internal degradation of excitation energy, and in this case it must be assumed that the presence of the supersensitizer permits the transfer of the excitation energy very rapidly, before it is converted to other forms in the dye molecule.

Mechanism of Spectral Sensitization

It is fair to say that the experimental evidence on spectral sensitization is extensive and that model systems, as well as photographic emulsions, have been used with good effect. It may now be said that substantial agreement has been reached on some points of its interpretation, although no complete theory of the process has general acceptance.

The basic concept which is accepted by most—although not all—of those working in this field is that excitation of the dye by light provides energy to elevate electrons to the conduction band of the silver halide; after this, latent-image formation proceeds in the same way as if the primary process had been absorption of light by the silver halide itself. This concept may be applied to more than one specific mechanism, and it will be best to summarize the evidence in its favor before discussing mechanisms. The most direct and conclusive evidence is that the relative spectral sensitivity of an emulsion is the same for photoconductivity and for photographic sensitivity. Added to this are the parallel effects of chemical sensitization in the regions of absorption of the silver halide and the dye, the relatively small differences of temperature coefficient between these regions, and the parallel reciprocity curves. All these are consistent with the concept that after electrons have reached the conduction band as a result of energy absorbed in either region, the secondary processes of latent-image formation take place with an efficiency determined, not by the primary process, but by the emulsion composition, chemical sensitization, and other environmental factors, including the presence of dye molecules in the ground state. It is perhaps conceivable that the facts would be as observed if sensitivity in one region depended on liberation of an electron by the primary process, and in the other on a photochemical change in the dye molecule to a product which could liberate an electron by a secondary chemical process, but it appears inherently improbable.

Oster has proposed[77] a mechanism of the latter type, based on experiments on sensitized photoreductions which indicate photoreduction of adsorbed

dyes as the primary process, but its applicability to the photographic emulsion is doubtful. Other proposals of this type have been made recently,[78] but on less evidence. Further discussion in this paper will be based on the hypothesis that the conduction electrons produced by exposure to light absorbed by the dye are the result of a primary process. The number of electrons appearing in the conduction band has not been experimentally compared with the number of quanta absorbed; it would be interesting to see how this ratio agrees with the value of φ_r for the system.

Because it is possible to recover dye after heavy exposures in which it has acted repeatedly to produce "print-out" silver, it is generally assumed that the dye is unchanged by the sensitizing process. This assumption is not necessary, because the number of silver atoms needed to form the latent image on a grain (not over 10^2) is vastly less than the number of dye molecules on the grain (about 10^5); but it is reasonable, because dye survives heavy exposures if protected by halogen acceptors. This implies either that the dye returns to its original state as soon as deactivated, or that it is regenerated by a rapid and efficient process. These alternatives correspond to the two mechanisms which have been most seriously considered: (1) Excitation energy transferred to the silver halide by a process analogous to collision of the second kind may lift an electron from a bromide ion to the conduction band. This process was formulated by Franck and Teller[79] in a form which has not been essentially changed since, and was considered in Mott's 1948 paper.[80] The excited dye molecule returns directly to its ground state on transfer of its energy to the silver halide. (2) An electron is transferred directly from the excited dye to the conduction band: this is the process suggested by Gurney and Mott in their first paper.[81] The dye is left as a free radical and must recover the electron or undergo further chemical change; but if the recovery is rapid, it will be difficult, if not impossible, to distinguish experimentally between this and the direct energy transfer; in fact, it does not seem that the distinction is of major importance or that either process must occur in all cases. There is a more valid distinction between the possibilities that electron transfer can occur only when the dye is in contact with a surface having occupied energy states above average, as assumed by Mott and most later writers, or that the dye alone may liberate an electron on illumination with visible light, as is implied by the photoconductivity data of Meier[65] and the recent work of Nelson[82] on sensitized photoconduction of glass.

A satisfactory mechanism for sensitization must be compatible with the energy requirements of the process. Since the sensitivity of pure silver bromide is negligible at wavelengths greater than 0.48 μ, there is no direct evidence of levels in the valence band less than 2.5 ev below the conduction band, and it is necessary to explain how smaller quanta may suffice to raise electrons to the conduction band. (This question, of course, arises in all systems where spectral sensitization occurs, although it is sometimes discussed as though it were a peculiarity of photography.) There is again quite good agreement on the general concept that the existence of intermediate levels between the top of the valence band and the bottom of the conduction band is necessary to sensitization. The numerical values involved are summarized in Fig. 4. The ground levels of sensitizing dyes are not known with certainty, and the results of measurements of ionization potentials, now under way, as announced at Liège, are awaited with much interest. Mott[80] quoted an estimate by Coulsen that the ionization potentials of cyanines are at 7 ev, but the basis for this estimate has never been published. Fleischmann[83] found a value of 5.5 ev for "cyanine Kahlbaum puriss" and it seems more reasonable to accept this value until better data are available, since his figure of 6.0 ev for silver bromide has been confirmed by later work. Quanta of 6500 A could just raise electrons from 5.5 ev to the conduction band of silver bromide; but sensitization of silver chloride to 8000 A, which can be done with good efficiency, would require 0.9 ev more than the 1.5 ev which are available for 8000 A.

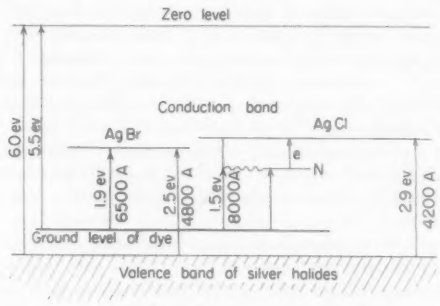


Fig. 4. Energy levels in spectral sensitization.

Sensitization of silver chloride to 8000 A would, however, be possible if the excitation energy could be transferred to a level N above the valence band from which it could lift an electron to the conduction band. The concentration of such levels, and the rate at which they could be replenished with electrons, might limit the efficiency of sensitization.

Thermal activation alone cannot be invoked to bridge the "energy gap," since this requires a temperature coefficient with a rapid systematic increase with wavelength, which has not been observed; the measured temperature coefficient is consistent with a barrier of the order of 0.1 ev, nearly independent of wavelength. Further data on temperature coefficient will be welcome.

Franck and Teller[79] suggested that "the energy transfer to the crystal can be delayed until the atoms in the crystal get into favorable positions." If the lifetime of the excited state of the dye is considerably longer than the necessary delay, the transfer process could be efficient and there would be little temperature effect. However, the lifetime of

an excited singlet state for a dye is of the order of 10^{-9} sec, and is small compared to that required for thermal fluctuations; this would appear to predict an inefficient process of high temperature coefficient. For this reason, the suggestion[84,85] that the excited dye passes into the relatively long-lived (10^{-3} to 10^{-4} sec) triplet state has been attractive in spite of the loss of energy. The transition to the triplet state, normally forbidden, is possible for dye adsorbed on salts of heavy metals,[85] and sensitizing dyes on silver halides have been shown by low temperature phosphorescence to possess triplet levels.[32] However, studies of the fluorescence of sensitizing dyes adsorbed on various substrates[86] have shown that the loss of excitation of dyes on silver halides takes place within the lifetime of the singlet excited state, so that it is quite improbable that sensitization normally takes place via the triplet state.

There is no question that, at defects, edges, and corners on the surface of silver halide crystals, there are energy levels above the normal valence band. It has even been suggested[87] that the change in the energy levels of both valence and conduction bands on approaching the surface brings them enough closer together to permit electron transition by long wavelengths, with low probability. When the surface is modified by chemical sensitization, with increase in depth of traps and with accompanying increase in long-wavelength sensitivity in the absence of dye, this might produce an increase in effectiveness of spectral sensitization; to date, chemical sensitization has been reported[39] only to increase sensitivity of a dyed emulsion by an equal factor at all wavelengths.[68] It seems probable that even primitive emulsion grains contain all the energy levels needed for spectral sensitization.

The specific mechanisms by which absorption by the dye can be used to produce transitions which have very low probability in its absence have been much discussed, especially in comparison to other unsolved problems. Mott[80] suggested that, since energy transfer between adjacent molecules of a dye layer may take place in 10^{-15} sec, the excitation could be passed through 10^{7} molecules in the 10^{-8}-sec lifetime of the excited singlet state, and the sensitization could occur if only a few of these molecules were in contact with a place where an electron could be freed by the available energy. The experimental evidence indicates that energy may be transferred very readily, from one dye molecule to another, to the point where it may be transferred to the silver halide; the alternative explanation is that energy may be transferred from any molecule, which is inherently less probable. The phenomena of anti-sensitization and supersensitization by small amounts of other compounds, and the fact that φ_r does not change with dye concentration in the absence of changes in aggregation, clearly indicate that all dye molecules are effective. The energy transfer between dye molecules will depend to some degree on the extent of the interaction between them. Where this is strong enough to produce a J-band, we have the classic example of exciton migration,[89] in which the time of excitation of an individual molecule is much less than the period of atomic oscillation. This appears to be unfavorable to transfer from the dye to the silver halide, and relatively low φ_r is frequent in J-band absorption; however, some dyes have φ_r values nearly 1.0 in the J-band state without supersensitization, and this has not yet been correlated with characteristics of the J-bands, such as halfwidth. Without J-band formation, transfer of excitation energy between dye molecules should still be possible by sensitized fluorescence;[89] the spacing of dye molecules in a saturated layer is about 4–5 A, whether a J-band is formed or not. In any case, it must be a state of excitation rather than ionization which is transferred between dye molecules.

The efficiency of dyes at very low concentrations, where a close-packed layer may not be formed, cannot be measured with precision, but there is no indication that it falls off. It is a reasonable assumption that dye will first be adsorbed at defects and other points where high energy levels are possible—an assumption which is supported by the higher heat of adsorption of the first portions. The dye layer should then build out from these areas, and dye should always be in contact with areas favorable for transfer. In the absence of better evidence, it seems impossible to decide whether the energy transfer between molecules must be replaced by a different mechanism in the final transfer to the silver halide.

The concept that the adsorbed dye is coupled to the surface levels of the silver halide is direct or implicit in the papers of Mott,[80] West,[32] Scheibe and Dörr,[90] Eggert,[91] and Mitchell,[92] as well as in the basic paper of Franck and Teller.[79] West[32] formulated the energy-transfer mechanism as follows: "If the difference in energy between the surface state and the conduction band is equal to the excitation energy of the dye, a resonance transfer can occur, analogous to an Auger transition in an atom, whereby the electron is excited from the surface state into the conduction band, while the dye reverts to the ground state." He has further (in private communication) pointed out the necessity for considering the dye–silver halide surface as a coupled system in which each part retains its energy levels, in order to allow for the very wide variation in sensitization by dyes having similar absorptions. If the dye is considered merely as increasing the probability of absorption at levels existing in the silver halide, there is no provision for such variation; but if the lifetime of the excited state in the dye and the probability of transfer to the silver halide surface level are still functions of the dye structure, the scheme has the required flexibility. The evidence available suggests that sensitization may be limited either by the rate of loss of excitation by internal degradation or by the probability of transfer. Comparing three 2,2′-cyanines,[86] West found that the nonplanar 1,1′-di Et-3,3′-di Me dye, which does not sensitize, did not fluoresce appreciably on any

substrate, presumably because of internal degradation; it will also quench the fluorescence of planar dyes of the same series. 1,1′-di Et-2,2′ cyanine, which is relatively inefficient, and a closely related dye which is about four times as efficient, are similar in their fluorescence on lead bromide, but the fluorescence of the better sensitizer is quenched more strongly by adsorption to silver bromide.

Mitchell[92] considered that the theory of dye sensitization proposed by Franck and Teller "is correct in its essential principles" and that the transitions in dye sensitization "occur between occupied energy states associated with surface halide ions and unoccupied states associated with surface silver ions." The low probability of these transitions is connected with physical separation of these states and is increased when they are bridged by the dye molecules, to put it in crude terms. Eggert[91] considers that the adsorption of either silver sulfide or a dye to the silver halide adds new levels to the upper edge of the valence band; sensitization occurs by electron transfer, with regeneration of the dye from a bromide ion at the same energy level. It is not clear why, if the electron can be transferred from the dye as a result of its association with the surface bromide ion, recovery of the electron from a bromide ion at this level should be regarded as a separate process.

Scheibe and Dörr[90] may be said to interpret the existence of sensitization as proving freedom of electronic interchange between silver halide and dye in the ionized state. Further support for this is given by earlier estimates by Scheibe that "in many organic molecules the ionization limit is quite close to 3.4 ev above the first excited level of the π electrons." This puts it close enough to the 3.5-ev value for silver bromide so that electron transfer by tunnel effect is possible. The intermediate levels in the silver halide in this scheme are essential to regeneration of the dye after loss of an electron, as in Eggert's description, but not for the first transfer.

The presence of dye molecules which have lost an electron should change the electron paramagnetic resonance of the system; attempts[32] to detect such a change have been unsuccessful, but the sensitivity of the measurements is likely to have been inadequate to differentiate between energy and electron transfer.

Terenin[61] considers that the evidence on sensitized photoconductivity obtained in his laboratory supports the energy transfer mechanism; the strongest argument is that *n*-type semiconductors, such as ZnO, and *p*-type, such as AgI and TlI with adsorbed iodine, may both be sensitized by dyes which are themselves both *n*- and *p*-type semiconductors.

In general, discussion of energy transfer vs. electron transfer has not led to any major advance in theory. Provided the basic energy levels of sensitizing dyes are in the vicinity of −5.5 to 6.0 ev, the energy-transfer mechanism appears to be adequate, and avoids a number of difficulties associated with electron transfer.

Scheibe and Dörr's discussion[90] includes an attempt to explain desensitization by sensitizing dyes in terms of the excited level of the dye. They conclude that this will be close to the bottom of the conduction band in any case, and that the direction of electron transfer between the conduction band and the dye will depend on small differences in level of the excited state of the dye relative to the conduction band, and on the concentration of free electrons in the dye layer and the silver halide. The theory that desensitizing dyes are those having vacant electronic levels below the conduction band of the silver halide has been suggested repeatedly and attempts have been made to connect it with oxidation-reduction potentials.

The most recent and important experiments are those of Tamura and Hada,[93] who calculated the lowest vacant levels of typical desensitizers having a nitrogen atom in the chain between heterocyclic nuclei, and of the thiacyanine series from 1 to 7 carbon atoms between the benzothiazole nuclei; the oxidation-reduction potentials of the thiacyanines were also determined polarographically and fell in the predicted order. According to their calculations, the bottom of the conduction band of silver bromide falls between the lowest vacant levels of the thiacarbocyanine (3-carbon chain) and thiadicarbocyanine (5 carbons). Measuring the change in sensitivity to violet light on bathing a chemically unsensitized emulsion with the thiacyanine dyes, they observed a sharp increase in desensitization from the carbocyanine to the dicarbocyanine. Their emulsion increased in contrast and sensitivity to violet light at the lower concentrations of the thiacyanines with 1- and 3-carbon chains; this is apparently a form of the "Capri Blue effect"[94] and complicates the interpretation of the results. In emulsions with normal chemical sensitization, desensitization by thiacyanine dyes increases continuously with concentration; the strength of desensitization increases with length of chain in the dye series, but there is no discontinuity between carbocyanine and dicarbocyanine.[37] Tamura and Hada observed desensitization at higher concentrations of thiacarbocyanine, and proposed a mechanism by which desensitization occurs in close-packed layers of dye but not at lower concentrations; however, such a change with concentration is not in agreement with experiment.

The prediction of the desensitizing properties of a dye from the relation of its lowest vacant level to the conduction band of silver bromide, or from its oxidation-reduction potential, is a more complete and quantitative version of the oxidation theory of desensitization, which probably applies to readily reduced dyes such as azines; but in the opinion of the writer, it cannot be a general explanation. In its simplest form, it predicts that dyes with their lowest vacant level above the bottom of the conduction band are sensitizers, and those below it are desensitizers, but it is now generally acknowledged that no such division of dyes into two mutually exclusive classes is possible; nearly all sensitizing dyes are, to a greater or lesser extent, desensitizers. Scheibe and Dörr[10] say that "it is also understand-

able that the same dye can act in some cases simultaneously as a sensitizer and desensitizer, as more electrons are driven into the conduction band by light absorption in the dye, or are captured by the dye from the conduction band after absorption of light by silver bromide." This would permit a dye to be a sensitizer for the red and a desensitizer for the blue, but it implies an inherent inverse connection between strength of sensitization and strength of desensitization which does not exist, and it does not seem compatible with the ability of a dye to desensitize for all wavelengths which the emulsion absorbs. Dr. Charles Duboc, of these Laboratories, has pointed out a further weakness of this concept. The excited level of the dye radical to which an electron has been added is unlikely to be the same as that of the uncharged dye, probably being higher. If it is higher, desensitization by transfer of electrons from the conduction band to the dye will be quite improbable.

There is the further question of the fate of the electron taken up by the dye; Scheibe and Dörr[90] suggest only that it is given up to an acceptor "for example, in the gelatin"; the fate of the holes is not mentioned, but they are presumably released as halogen. If energy transfer is statistically reversible, dye molecules may become excited, with return of an electron from the conduction band to the surface state with which the dye is coupled; the excited dye then may degrade the energy. Either way, desensitization will depend on the combined probability of transfer of energy or an electron to the dye, and of loss of the energy or electron in a way which does not produce image. It does not seem conceivable that, if such a desensitizing process is probable in a dye, there should also be a high probability that the excited dye should readily transfer an electron or energy to form image, but dyes are known which combine high φ_r with strong desensitization.

It seems much more likely that desensitization depends on means for inducing recombination of electrons and holes. This should be the case if dyes are traps for positive holes, at which recombination of the hole and the electron is facilitated. It is well established[95,96] that many sensitizing dyes add bromine reversibly, and that the bromine addition products are strong desensitizers. This is not proof of hole trapping, as the dye may be adding molecular bromine across a double bond, but it is a reasonable assumption that the dye in the ground state may capture holes, and that recombination of electrons with the trapped holes is facilitated. Mitchell[92] has pointed out that recombination at traps is the normal case, in contrast to the situation in silver halide where a trapped electron may be protected against recombination by charge effects. Such a mechanism of desensitization (1) is independent of the wavelength of exposure and the excitation of the dye, (2) has no direct relation to the sensitizing efficiency of the dye, (3) may vary widely with the chemistry of the dye, (4) does not further require the presence of an efficient electron acceptor. The presence of halogen acceptors might still cause some reduction of desensitization, and such effects have been reported,[97] but the effectiveness of the dye for desensitization will depend on its ability to trap single positive holes rather than on its reaction with molecular halogen. Further experimental tests seem possible. It should be noted that Tamura and Hada[93] propose recombination of electrons trapped in the dye aggregate with holes; the distinction between the proposed mechanism and theirs is that the dye is more likely to trap holes than electrons and that desensitization is not dependent on aggregation of the dye.

The efficiency of sensitization depends on the emulsion conditions, and the possible variation (best measured by φ_r) is of the same order as the variations caused by dye structure. Some of the effects fit readily into the general scheme already outlined. Antisensitization is explained satisfactorily by transfer of excitation through the dye layer to the antisensitizer, which must be capable of being excited to its singlet state by the singlet state of the planar dye, as shown by the wavelength relations; the excitation energy is then degraded by the nonplanar dye. Since transfer of energy through the dye layer to supersensitizer molecules is probable, explanations of supersensitization depend on mechanisms by which transfer to the silver halide at the discontinuity produced by the supersensitizer molecule is easier than elsewhere in the dye layer. Simple transfer of energy from singlet state of the dye to singlet state of the supersensitizer, with transfer from the supersensitizer to the silver halide, is impossible as a general explanation, because the supersensitizer may absorb at shorter wavelengths than the dye supersensitized. There are the further difficulties that supersensitization in a mixture of two dyes is often mutual, and that supersensitizers are not as a class outstanding sensitizers.

Brünner, Oberth, Pick, and Scheibe[74] have obtained evidence for transfer of excitation energy to the triplet state of the supersensitizer; the phosphorescence bands of four compounds indicated that their triplet levels were below or above the singlet levels of dyes as predicted from their positive and negative effects as supersensitizers of the dyes. Supersensitizers quench the fluorescence of dyes which they supersensitize,[72] as would be predicted if they take energy from them. Against this is West's[32] failure to excite the triplet levels of supersensitizers when they were mixed with dyes which they supersensitized, and the mixture exposed to light absorbed by the latter dyes. It should also be noted that it is necessary to assume that transfer to the supersensitizer from the singlet level of the dye supersensitized is easier than from the singlet level of the supersensitizer to its own triplet level; otherwise the latter would consistently be the stronger sensitizer. There seems to be no theoretical reason against this, but altogether the intervention of the triplet state in supersensitization, when generally it is not as efficient as the singlet in sensitization, is difficult to accept.

Mitchell[92] postulates adsorption of the supersensitizer "along and parallel to the edge which produces the discontinuity in the aggregated monolayer of dye," but the present writer is unaware of any evidence that typical supersensitizers should be adsorbed at points where dye is not.

West and Carroll[63,72] suggested that the supersensitizer represents a discontinuity in the dye layer which confines the migration of energy to a shorter path. Since supersensitizers normally become part of the layer, as indicated by disappearance of their characteristic absorption, but do not destroy the J-band until present in high proportions, their role as singularities is reasonable. Increased transfer probability at such a singularity may be postulated simply as the result of an increase in the time when the energy is localized. Mott[80] stated this as the possibility that the supersensitizers "act as traps for excitons." It has not been possible to relate this to the properties of the supersensitizer, except that it must be sufficiently different in structure to produce a discontinuity in the mixed dye layer. In short, the hypothesis, that supersensitization occurs by transfer of the excitation energy to the supersensitizer and thence to the silver halide, is the simplest but there is little experimental support for the required processes; it seems more probable that the presence of the supersensitizer facilitates transfer from the other dye to the silver halide, but no specific explanation for this is known.

Increased silver-ion concentration in the emulsion (hypersensitization) has a small positive effect on photographic sensitivity, as is to be expected if the mobile silver ions on the grain surface are in equilibrium with the rest of the system, and the rate of arrival of silver ions at sensitivity nuclei is a factor in the probability of image formation vs. regression. The effect is largest in silver iodide, which has the greatest tendency to regression.[97] In the presence of dye, the effect of silver-ion concentration on sensitivity in the violet is greater than in the unsensitized emulsion, and there is a further increase in the region of spectral sensitization, corresponding to an increase in φ_r. The magnitude of the effects varies widely with the dye, and not enough data are available to correlate them with the most obvious possibility, the desensitization by the dye. If desensitization is a regression effect—and it seems that it must be—it should be reduced by making more silver ions available, provided this is to any extent a "bottleneck" in image formation; however, it is not clear why this should do more good to sensitivity to light absorbed by the dye than to sensitivity to light absorbed by the silver halide.

Summary of Discussion

There is good agreement that:

(1) Spectral sensitization occurs by a primary process in which the excitation energy of the adsorbed dye is used to raise an electron to the conduction band of the silver halide; the secondary processes are then the same as when the energy is absorbed by the silver halide. However, rates and efficiencies of secondary processes may be modified by changes in emulsion environment, such as the presence of the sensitizing dye.

(2) Surface states in the silver halide take part in the process of latent-image formation by quanta smaller than those absorbed by the silver halide itself.

The question whether the primary process occurs by transfer of an electron or energy from the dye molecule is still open, but probably academic. The relations of the chemical and physical properties of a dye, other than its spectral absorption, to its characteristics as a sensitizer or supersensitizer are relatively unknown. It is suggested that desensitization depends on the ability of a dye to trap holes and facilitate their recombination with electrons.

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An Advanced Technique for Short Delay Processing of Photographic Emulsions

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A simple and reliable new method for the controlled application of processing liquids to the emulsion surface of photographic film utilizes a porous applicator for each processing step. The applicator forms a stable meniscus over a controlled area on the emulsion surface of the moving film. The processor is compact and simple and yields high-quality processing with a large assortment of available emulsions and chemicals. Sensitometric results for several emulsions and processing conditions are presented, and possible uses and future potential are discussed.

The processing of photographic film consists of a series of chemical reactions between substances held within the gelatinous structure of the film emulsion and substances contained in the various solutions brought into contact with the film. The speed at which these chemical reactions take place increases, as in most other chemical reactions, with the temperature at which the process takes place. It is this principle which permits film processing time to be significantly reduced from that required at the usual temperature of 68°F.

A number of limitations to the maximum temperature at which a process may be maintained prevent indefinite reduction of processing time. Some of these limitations are manifested through chemical fogging, separation of emulsion from base, and oxidation of the processing chemicals. A broad spectrum of automatic processing equipment has been devised to bring the processing chemicals and film emulsion together under conditions where precise control may be maintained over all parameters. With such devices, it is possible to take maximum advantage of time reduction techniques without danger of exceeding the prohibitive limits.

It is the purpose of this paper to describe in detail a system with which the processing chemicals are applied to the film emulsion while maintaining complete control over the process temperature and the time of contact between the film and successive solutions. A simple direct approach is employed which can utilize a wide assortment of film and chemical combinations to produce good quality photographic reproductions and which lends itself to integration into a system for minimizing the film processing-cycle time.

Background

Photomechanisms, Inc., under subcontract to Eastman Kodak Company, during the past four years has revived and developed to a high degree, for use in military airborne radar recording equipment, the relatively old technique employing a porous applicator for wiping successive processing chemicals onto the emulsion surface of moving film.[1] In a camera-processor using 9.5-in.-wide film,[2] a porous rotating roller applicator is employed to produce a high-resolution continuous-tone radar map seconds after the aircraft has passed over the recorded area.

The Rapidata* principle was first employed in an airborne 35mm camera-processor in which complete development and fixation of the film were required, in order to permit the photographic record to be electronically scanned. Two stationary porous applicators of sintered stainless steel were mounted on manifolding blocks instead of on the roller used previously. A meniscus was formed between the top surface of each porous applicator and the downward-facing film emulsion, permitting the film to contact first the developer and then the fixer. A stabilized developer of the monobath type was used to permit varying the film rate while maintaining consistent processing results. The separate fixation stage used a component with sufficient chemical activity to clear the film at the maximum film speed.

Detailed Description of Present System

A recent embodiment of the shoe-type porous applicator processor is contained in a demonstration model camera-processor-viewer which has been displayed on many occasions over the past year. A schematic representation of this device is shown in Fig. 1. It may be seen that the film processor is inserted, with very little lost space, between a camera portion and a viewing station using a U-shaped film path enclosed within the body

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* Trademark of Photomechanisms, Inc.

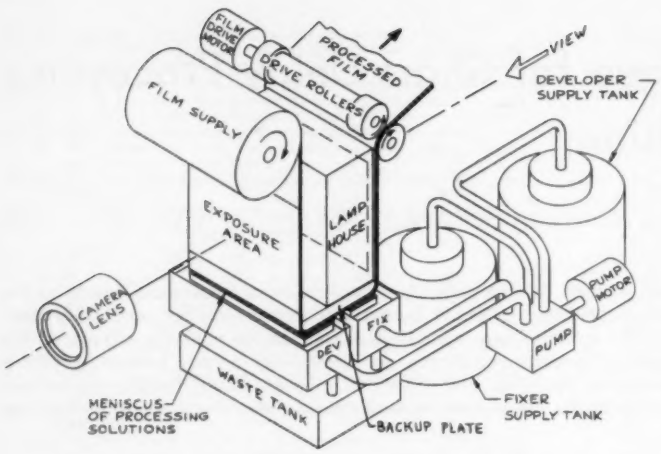


Fig. 1. The Rapidata Photo-Processor System.

of a relatively small piece of equipment. Each component of this system is described below in some detail.

Film. Delay time between exposure and viewing may be minimized by elevating the temperature of the process beyond the recommended values. Prehardened emulsion films have been processed quickly and with good results at temperatures of 130°F or higher. Examples of films successfully processed at 130°F include Ansco Hyscan, Eastman Kodak SO-264, Recordak Dacomatic, and Du Pont 931. While these films are hardened to withstand elevated-temperature processing, it has been found that the Rapidata principle permits standard films to be processed at temperatures considerably above the recommended 68°F without suffering physical damage or significant loss in quality.

When minimum delay time is not of prime importance, and it is desired to simplify the processing procedure and minimize the equipment required to achieve high-quality processing, standard films may be used at standard or moderately elevated temperatures. Fast and thick emulsion films may be processed by this technique, provided the time and temperature of the process are adjusted to avoid exceeding the physical limits of the film emulsion.

At present, no techniques are offered for the removal of dye from backed film. However, it is believed that dye removal could be accomplished by treatment of the film back with chemicals applied with a porous applicator.

Processing Chemicals. In certain special applications, high-energy developers balanced for use at an elevated temperature are required. When the film rate must be varied, a stabilized or arrester developer is required to produce uniform sensitometric results. A fixer component suitable for short clearing time at elevated temperatures is usually necessary. The most severe restriction on the fixer component is the requirement for either no deposit or a specularly clean deposit of residual chemicals. The Kodak monobath designated PS-497 and its concentrated fixer component have proven highly satisfactory for military applications.

Processing chemicals must be chosen with particular attention to the problems encountered when developer is carried into the fixer and to the physical characteristic of the fixer residue on the film. In addition, many developers cannot stand an elevated temperature without causing severe fogging.

In many applications stabilizing solutions are adequate in place of a true fixer. With stabilizers, the film may be cleared in a short time and image stability maintained for a period of many months. One such successful stabilizing solution used consists of a mixture of a solution of thiourea and acetic acid.

Another answer to the fixer residue problem was found when a third applicator head was added to the processor. This head applied a meniscus of warm water to the moving film. The excess residual fixer was largely removed, preventing a crystalline deposit from forming. This cannot be considered an adequate wash, but the resulting film is sufficiently clean to permit specular optical sampling when using a standard rapid liquid fixer.

All the graphs shown in this paper contain curves of films processed by the two-step method, using porous applicators for both solutions. Fixer or stabilizer was used to clear the film. Most samples were washed briefly and dried before readings were taken. Several graphs include a curve of the film tray processed for comparison.

Film Drive. The film is advanced at a uniform rate through the processing station. Film may be used with or without perforations by employing rubber-covered pinch-drive rollers. No special care is required to maintain a high degree of uniformity in the film velocity through the processing station. In systems where the film motion represents one scan direction of a two-dimensional photographic image, as in side-looking radar, the same drive may be employed for both the scanning and the processing functions. In some cases, long-term frame-by-frame relationships must be maintained with sprocket devices.

The drive roller on the emulsion side of the film may be undercut to bridge the exposed and the processed area. This permits handling the film by contact with only the dry margins and avoids the smudging of the chemical deposit on the processed surface of the film. The drive rollers thus operate dry and the problems that result from having moisture on the rollers are avoided. It is desirable to maintain tension on the film in the processing station in order to hold it taut and properly formed over the back-up plate. In this way the gap between the emulsion and the applicator shoe may be predicted and maintained within close tolerances.

In some devices a servo-controlled variable-speed film drive is required to permit adjustment of the film

rate to a given value, such as the aircraft ground speed in the case of side-looking radar. In the demonstration model Rapidata photo-processor, a variable-ratio gear reducer is used to permit manual adjustment of film velocity.

Pump. A simple constant displacement pump, comprising the only moving part of the processing system, is used to maintain a constant solution flow rate through the applicator. This pump is of the peristaltic type, requiring no seals or contact of chemicals with metallic parts. The pump operates by an eccentric roller squeezing a turn of rubber tubing against the inside surface of a cylindrical housing. As the roller advances, the squeezed portion of the tube forces the solutions ahead. Several tubes may be paralleled, permitting a single pump to handle many solutions simultaneously. The pump may be driven with the film drive motor to meter solutions at a rate proportional to film speed. Many hundreds of hours have been logged on this type of pump without failures.

Solution Tanks. The processing solutions may be supplied in premixed packaged form, with plug-in type connectors for convenience in handling. Alternatively, stainless steel tanks may be utilized with vented screw-in caps, depending on the need of the particular user. The exhausted solutions are collected in a waste container which may be emptied at intervals or disposed as the particular case may require. The tanks may be remote from the processing equipment itself for convenience in system packaging and may be of any capacity required for a specific operation.

Back-Up Plate. For wide-film and paper-base materials, it has been found that drawing the material tightly over a curved plate permits the emulsion to be held in a predictable cylindrical surface. Without this aid, wide materials tend to buckle when they come into contact with a heated processing solution. Buckling causes nonuniform spacing between the emulsion and the processing head, resulting in severe streaking, and often causes the emulsion to be rubbed off when it comes into contact with the applicator head. Films of 35mm width and narrower do not suffer from this buckling tendency and may be utilized with a flat back-up plate to conserve space and reduce cost of fabrication.

Rollers may be employed for this purpose, but the diameters become rather large when a few inches of applicator length along the film are required. In the radar recording application for military systems previously constructed, rollers were used with great success. In these cases, the meniscus length was approximately 0.060 in. In the system shown in Fig. 1, approximately 1 in. of meniscus length can be obtained in each of the developing and fixing stations by using a fixed back-up plate. The use of rollers here is not practical because of the large size required.

To maintain the elevated temperature at which the process must take place, a thermostat and a set of heaters have been included in the back-up plate. This has resulted in considerable improvement over the control of the process temperature. In some cases, the back-up plate has supplied all the heating means for the process. This has the advantage of maintaining a low fog level with certain types of developers. The back-up plate temperature is usually kept at the same level as the solution manifolds.

Applicator. Figure 2 illustrates the pertinent features of the applicator. A $^1/_8$-in.-thick porous plate, made from

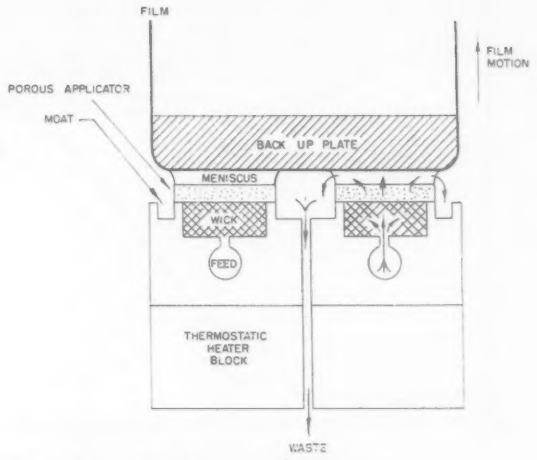


Fig. 2. Cross section of porous applicator processor.

sintered stainless steel granules, is cut to the width of the exposed area on the film and to a length generally determined by the required film rate. It has been found desirable to limit the processing head to approximately 1 in. in length, and build up as many 1 in. modules as required for a particular length. In this case, a single head was utilized for each of the two processing solutions. The stainless steel plates are fastened to a manifold block which contains a feed pipe and a cavity containing a Dacron wick material. This aids in dispersing the solution flow uniformly through the porous material.

A pump rate is maintained which slightly exceeds the rate of solution carry-off, thereby forcing the meniscus to bulge slightly on all four free boundaries. The excess solution flows down the edge of the porous shoe from the boundaries of the meniscus, and is collected in a moat around the shoe. From there, it is drained by gravity or pumped into the waste tank.

By means of cartridge heaters, the thermostatically controlled manifolding block is heated to the temperature desired in the process. The solution flow rate is slow enough to permit the solutions to reach the temperature of the block before coming in contact with the film.

Recently an even simpler head design has been tested successfully. In it, the chamber containing the wick is eliminated and the porous plate accomplishes the dispersion of the solution flow.

It can be seen that the drain of waste solution is the major reason for maintaining a particular orientation of the processor head. Gravity is depended upon to draw the excess solutions away from the film and prevent them from spreading outside the meniscoid boundaries. The drainage system, however, can be designed to permit proper functioning at severe departures from the normal operating position.

The Gap. The spacing between the film emulsion and the processor applicator is set to maximize the stability of the meniscus. This spacing depends in part upon the viscosity of the liquid used in the processing materials. A properly adjusted gap will work equally well with any aqueous solution within a limited range of film velocities. It has been found that at higher velocities in the range of 20 to 30 in./min, the gap must be reduced to maintain

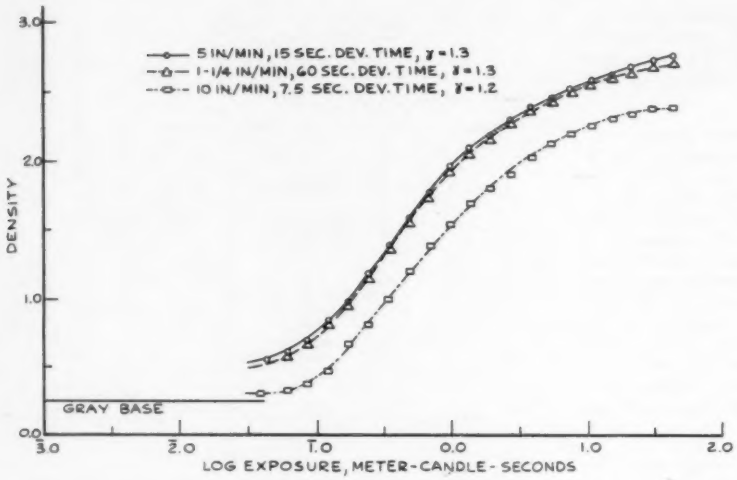


Fig. 3. Development of Kodak SO-264 Film in Kodak PS-497 Monobath at 130°F.

stability. For aqueous solutions, the gap averages approximately 0.010 in. Adjustment for proper operation of this spacing constitutes the most critical parameter in the system. Its setting can be adjusted by experimentation, then measured and set in subsequent similar units without further need for experimental adjustment.

Of particular significance is the fact that no solid objects come in contact with the exposed and processed emulsion at any time. This permits soft emulsion films to be processed at moderately elevated temperatures without suffering physical damage.

Performance of System

The Rapidata technique does not affect the processing chemistry in any noticeable way: it merely brings the film and chemicals together under controlled conditions. The processing time for each solution is determined by dividing the length of the particular processing head by the film velocity. The temperature is thermostatically controlled in the heating of the solution manifold and the film back-up plate. It appears from the results that the constant feed of fresh solutions and the shearing action within the meniscus constitute good agitation.

The laboratory equipment utilized to generate the curves is similar to that shown in Fig. 1. It possesses two applicator heads, each about 1 in. long. The two porous shoes are spaced about 0.25 in. apart. A low-velocity warm-air-impingement drying technique was employed.

To date no sensitometric study with statistical averaging has been made of the process with a defined set of film and chemicals. However, a number of exploratory tests have been and are being run in an attempt to determine the areas in which detailed sensitometric analysis should be concentrated.

The greatest amount of information has been collected with the blue-sensitive prehardened cathode-ray-tube recording films which are intended for processing at elevated temperatures. Most of the applications in which these films were employed utilized a stabilized developer of the monobath type to permit variation in film rate without noticeable variations in the sensitometric results. Typical sensitometric results using Kodak SO-264 film and Kodak PS-497 monobath are shown in Fig. 3. Three runs in the same device under identical conditions were made at 1.25, 5 and 10 in./min.

The three curves show similar characteristics over nearly 10:1 range with only a small drop in the entire 10-in./min curve. The total processing time at the highest rate is about 10 sec. The processor was run at 130°F, the temperature recommended for the materials used.

Figure 4 shows the 5-in./min curve of Fig. 3 for comparison with a pair of curves run on SO-264 film processed in D-19. One was tray processed at 68°F for 8 min, the other processed with porous applicators at 1.25 in./min at 76°F. The developing time with the porous application was only 60 sec, but the maximum density is comparable to that obtained by the other two methods. While the film speed has suffered slightly, the gamma has not, and the chemical fog is very low.

Ansco Hyscan, a film similar to SO-264, was tray processed with D-19 for 8 min at 68°F and run at 5-in./min at 130°F with the PS-497 monobath. These two curves are shown in Fig. 5. The high temperature has raised the fog level but maintained comparable performance elsewhere.

Curves for a third prehardened film, Du Pont 931, processed under three different conditions are shown in Fig. 6. One sample received the manufacturer's recommended processing. The others were run in the Rapidata Processor, one at 10 in./min with the Kodak PS-497 monobath and the other with D-8 at 100°F at 5 in./min. Note that the fog level and speed are down while gamma is up with the D-8 developer.

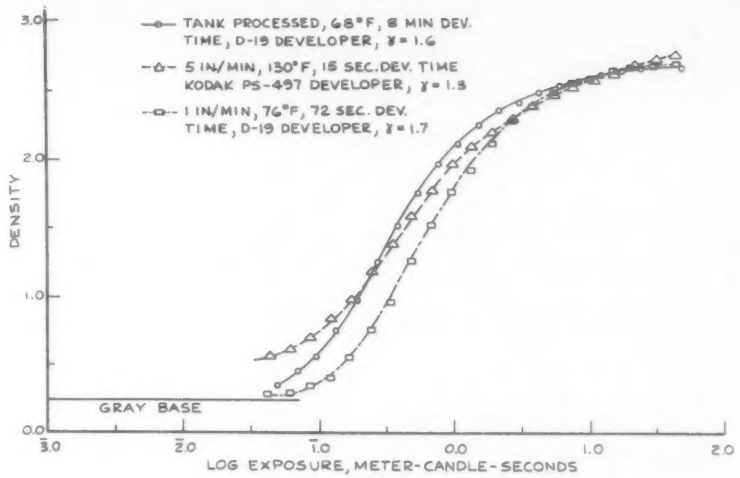

TANK PROCESSED, 68°F, 8 MIN DEV. TIME, D-19 DEVELOPER, γ = 1.6
5 IN/MIN, 130°F, 15 SEC. DEV. TIME KODAK PS-497 DEVELOPER, γ = 1.3
1 IN/MIN, 76°F, 72 SEC. DEV. TIME, D-19 DEVELOPER, γ = 1.7
GRAY BASE
DENSITY
LOG EXPOSURE, METER-CANDLE-SECONDS

Fig. 4. Development of Kodak SO-264 Film.

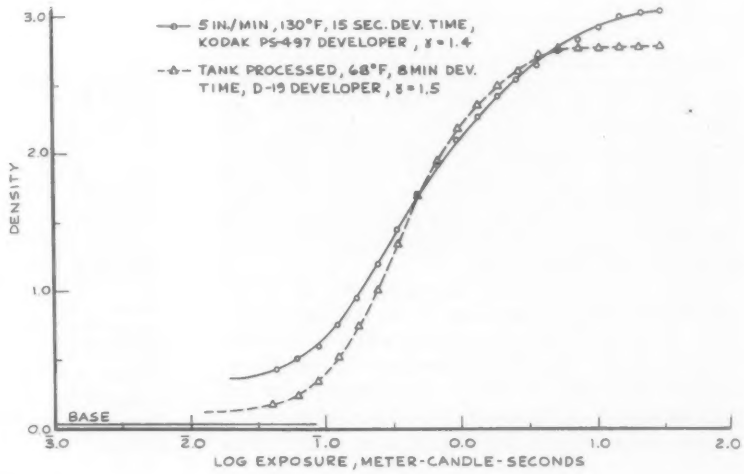

5 IN./MIN, 130°F, 15 SEC. DEV. TIME, KODAK PS-497 DEVELOPER, γ = 1.4
TANK PROCESSED, 68°F, 8 MIN DEV. TIME, D-19 DEVELOPER, γ = 1.5
BASE
DENSITY
LOG EXPOSURE, METER-CANDLE-SECONDS

Fig. 5. Development of Ansco Hyscan Film.

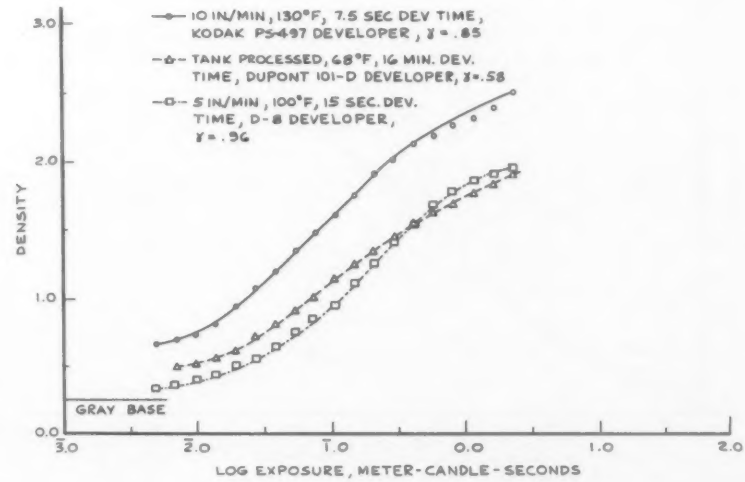

10 IN/MIN, 130°F, 7.5 SEC DEV TIME, KODAK PS-497 DEVELOPER, γ = .85
TANK PROCESSED, 68°F, 16 MIN. DEV. TIME, DUPONT 101-D DEVELOPER, γ = .58
5 IN/MIN, 100°F, 15 SEC. DEV. TIME, D-8 DEVELOPER, γ = .96
GRAY BASE
DENSITY
LOG EXPOSURE, METER-CANDLE-SECONDS

Fig. 6. Development of Du Pont 931 Film.

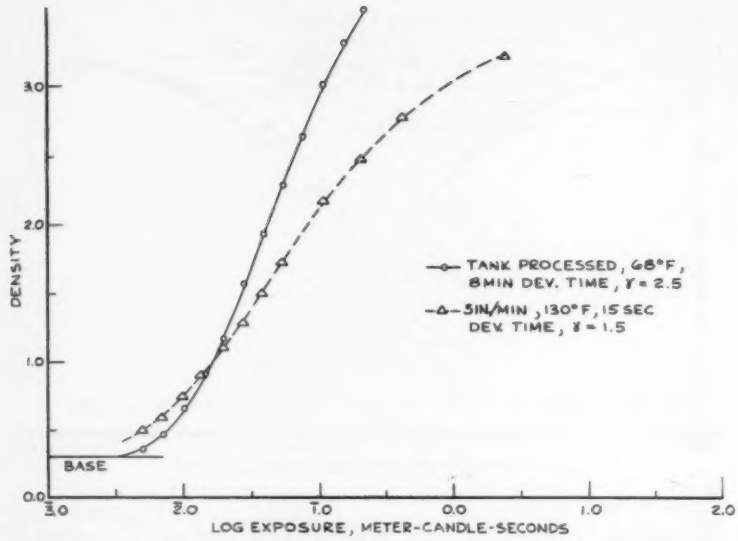


Fig. 7. Development of Linagraph Shellburst Film in Developer D-19.

Figures 7, 8, and 9 show other film types which are not hardened for high-temperature processing. In Fig. 7, Linagraph Shellburst is shown processed with D-19 at 5 in./min at 130°F in the Rapidata and for 8 min at 68°F in the tray. The increased fog and reduced speed, gamma, and D_{max} of the former are to be expected from the increase in temperature and reduction in time. Developing time with the porous applicator was about 10 sec.

Figure 8 shows remarkable agreement in results with Kodak Plus-X processed in the Rapidata in D-19 for 60 sec at 78°F and in a tray with Microdol for 7 min at 68°F. The Plus-X emulsion blistered and came off the base at 130°F. No attempts as yet have been made at intermediate temperatures.

Curves for Kodak Tri-X processed under three different conditions are shown in Fig. 9. With D-19 at 130°F, the film can be processed in a total of 30 sec at 5 in./min, with relatively high minimum density. The results of tray processing in DK-60A for 3.75 min at 68°F are roughly comparable to processing in Kodak Monobath PS-497 at 1.25 in./min in the Rapidata maintaining 76°F temperature.

From these preliminary investigations it can be seen that the porous applicator technique can make a definite contribution toward simplified high-quality short-delay processing. With film and chemicals properly chosen for use under the conditions of porous applicator processing, highly favorable sensitometric results may be obtained. The approach provides a means for combining film and chemicals in ordinary forms where precise control may be held over all conditions.

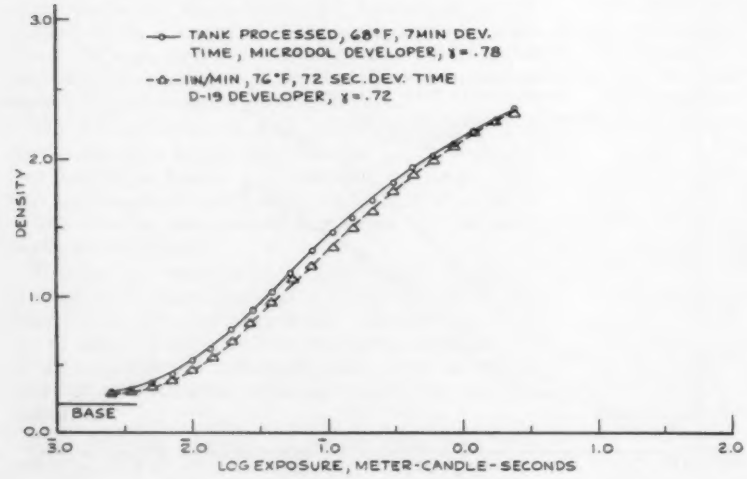
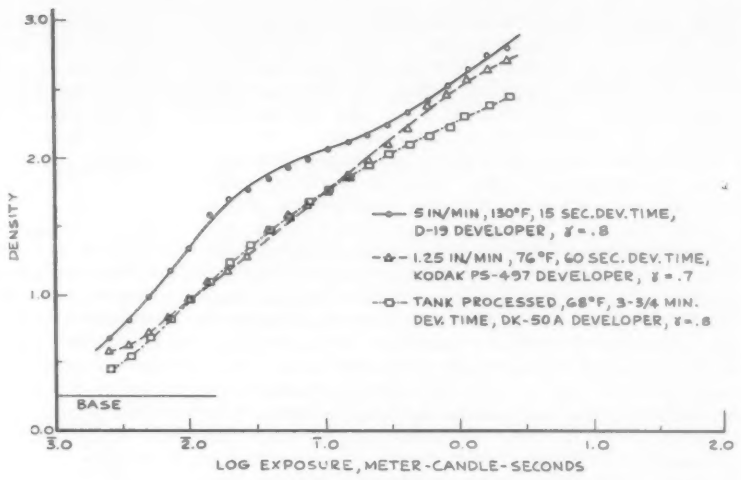


Fig. 8. Development of Kodak Plus-X Film.

Fig. 9. Development of Kodak Tri-X Film.

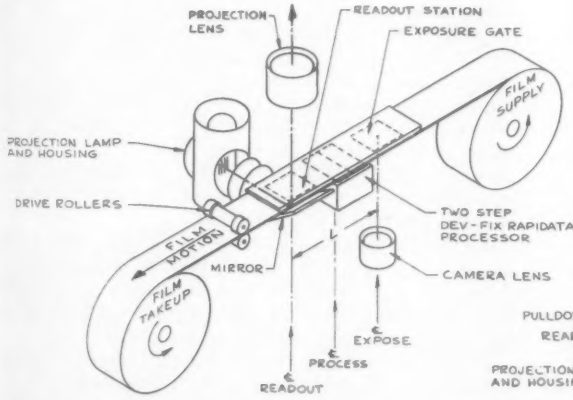


Capabilities for System Integration

Two basic parameters are generally of interest when considering the possibilities for integration of a Rapidata Processor into a system. These are: (a) the delay time between completion of exposure and start of readout, and (b) the film velocity.

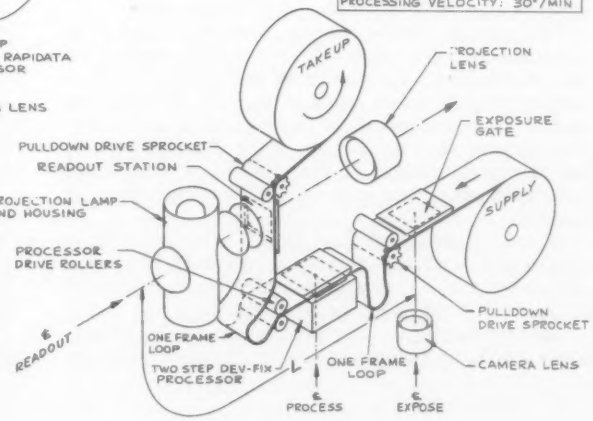
Often the delay time must be minimized. The basic minimum delay-time parameter is determined by the chemical reaction time of the process at a particular temperature. With the Kodak PS-497 solutions operating at 130°F on Kodak SO-264 film, the chemical time totals approximately 5 sec for developing and fixing.

In a system where low film velocity is required, such as in side-looking radar, it is desirable to maintain a short processing head dimension along the axis of the film. The practical lower limit to this dimension may restrict the minimum delay time for extremely low film velocities. At present, it is believed that the practical minimum for each processing head is approximately 0.25 in. For this head length, a maximum speed of approximately 0.1 in./sec is imposed by the chemical limitations, with a



PARAMETERS	35 MM FILM	70 MM FILM
FORMAT	1X1"	2.3X2.3"
PATH LENGTH, L	3.4"	4.7"
TIME DELAY	6.8 SEC	9.4 SEC
PROCESSING STATION LENGTH: 2.4"		
PROCESSING VELOCITY: 30"/MIN		

Fig. 10. System configuration for minimum delay time.



PARAMETERS	35 MM FILM	70 MM FILM
FORMAT	1X1"	2.3X2.3"
PATH LENGTH, L	6.4"	7.7"
TIME DELAY	12.8 SEC	15.4 SEC
PROCESSING STATION LENGTH: 2.4"		
PROCESSING VELOCITY: 30"/MIN		

Fig. 11. System configuration for minimum delay when storage loops are required to permit rapid pulldown of the frame.

total delay of about 6 sec available due to the requirement for a small space between the heads. However, at lower film velocities, the time delay is increased to the time required to traverse the head lengths. For example, at a film velocity of 0.05 in./sec, a delay time of 12 sec results.

For higher film velocities, it is possible to maintain the minimum delay time imposed by the chemical process by increasing the head lengths of the applicators. For example, for a film velocity requirement of 1 in./sec, each processing head would have to be 2.5 in. in length. The upper limit to this type of extension is not as yet known. It has been found that it is desirable to break the applicator shoes into segments of not more than 1 in. to avoid accumulation of expended solutions in the meniscus. This same concept can be extended into processing of standard film and chemicals at appropriate temperatures and times. For example, Tri-X may be processed at 70°F for 5 min each in the developer and fixer selected by utilizing two 2.5 in. processing heads and transporting the film at the rate of 0.5 in./min.

Figure 10 depicts a method by which minimum-delay frame-by-frame recording and readout may be accomplished. Minimizing the spacing between the successive stations is of prime importance.

While the processing system itself requires continuous film motion through the processing station, it may be integrated into systems which require frame-by-frame recording and readout modes of operation. Figure 11 shows an example of a possible system in which film is exposed in a frame-by-frame sequence forming a loop between the exposure and the processing stations. The film is intermittently moved through the exposure station and continuously moved through the processing head. A similar arrangement may be employed between the processor and the readout station, permitting projection of a previously processed frame of information until the next one has been completely advanced into the storage loop. Then a rapid pulldown in the projection station may be employed to minimize the delay between adjacent projected frames.

The capacity of the storage loops may vary from one frame to many hundreds of frames, depending on the requirements for recording and readout. In a random exposure rate application, such as computer readout, the processor may be designed to accommodate film at the average rate while the pulldown in the recording station is designed to accommodate the maximum frame rate which the computer may demand.

In most systems of these types, it is desirable to advance the last frame which was exposed through the processor into the readout station before shutdown of the unit. In this way, unexposed film is left in the processing station for the extended periods of shutdown. It is undesirable to leave recorded information in the processing station during the shutdown due to the tendency for chemical fogging to take place and for the film base to absorb moisture and swell. In cases where holding recorded information in the processing area cannot be avoided, it is possible to drop the processing head away from the film surface.

Future Potential

The system described here is still in the early stages of development. The process is being used with great success for development of film and paper in widths from 35 mm to 12 in. It lends itself extremely well to two major areas of application:

(a) where requirements call for short delay between exposure and readout of continuously moving film through high-quality processing in a minimum of space and equipment complexity;

(b) where a simple, direct, inexpensive, reliable means for good quality processing with standard materials is required.

In the areas of high-speed data display, storage, retrieval, and duplication, and in most military applications, the short delay time is of prime importance. With some changes, it appears practical to utilize the principles of porous-applicator processing in a satellite or other nongravity environment. At present, the known restrictions against its use under these conditions are in the area of removal of waste solution.

A small simple table-model film processor which utilizes this approach also appears to have a great many applications. The equipment can be inexpensive and will obviate the need for a darkroom facility for routine processing of strip films. Furthermore, it makes unnecessary the lengthy delays associated with sending films to processing specialists. The rate of solution consumption is very low—of the order of 0.25 cc each per square inch of film—regardless of width or length involved. In addition, since standard materials may be used, the cost of photographic recording is minimized.

Developments in the areas of cut-film and glass-plate processing are under serious consideration. Also, the application of this technique to amateur film and print processing appears practical with black-and-white, reversal, and color materials.

The success of this simple, direct approach in providing reliable and convenient photographic processing opens the way for many new uses of the photographic recording medium previously considered impractical. The Rapidata system permits retrieval of photographically recorded information with ease nearly equivalent to that of magnetically recorded data.

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Quick Processed Bright Displays by Xerography

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A family of methods is presented for creating bright displays in seconds by means of xerography. The displays are characterized by high brightness, good definition, and good contrast. In one such system, a cathode-ray tube image is projected onto a charged xerographic plate to create the latent electrostatic image. The plate is then developed with a charged powder and instantly illuminated with a focused beam of light which is specularly reflected at high efficiency from the plate surface and imaged by a lens to create the display. This has been called PROXI, for "Projection by Reflection Optics of Xerographic Images."

When the image is no longer needed, the powder can be brushed from the plate so that the latter is ready for re-use many times, or it can be transferred, as in commercial xerographic copying, to a sheet of paper for record purposes. The system is most suitable to console-type displays. In other proposed xerographic systems the powder image is transferred prior to projection in order to achieve final luminous flux levels suitable for large screen displays.

The projection of an optical image onto a screen, whether as a still or a motion picture, has long been a means of audience entertainment. More recently, the art has been called upon to assume the even more responsible role of educating for information and enlightenment.

The growth in the use of projected visual materials has been possible largely because of readily available photographic techniques, cameras, transparencies, and films. The use of opaque materials in projection systems, on the other hand, has been limited to a few applications in education and business, because such subjects do not conveniently lend themselves to large bright display. Pictures on paper have, therefore, remained materials for personal direct viewing, while transparencies and films have become the media for mass communication.

Despite the wide use of photography in creating visual displays, there are many instances where it leaves much to be desired. For example, when the time lapse between data input, in the form of exposure to a light image, and projection of the recorded information to a screen must of necessity be very short—perhaps 1 to 2 sec or less—then the photographic process becomes complicated and expensive. Quick displays of electronic data can, of course, be made by television and direct-view storage tube systems, but the ultimate screen size and brightness of the display are severely restricted.

With the advent of supersonic aircraft and missiles, military systems require new techniques for high-speed data collection and display. Some of these methods involve projecting visual data of many types onto a screen which can be viewed by planning personnel. The information may be stored in tables or charts, or in electronic computers, and the data must be processed rapidly and projected onto a screen for viewing.

Similar applications may well exist in the business world. The executive who wishes to review data contained in a filed document, so that a decision can be made, would welcome a fast, efficient, and low-cost system for data retrieval and presentation.

Through newly devised techniques, the xerographic process has been adapted to produce a bright display of input data in the form of an optical image. Of prime importance is the fact that the time lapse between exposure and projection can be as short as 1 sec or less.

The Xerographic Process

Xerography is a photoreproduction process based on physical rather than chemical phenomena.[1] A re-usable photoconductor which is not damaged by exposure to light, radioactivity, or ionizing radiation is first sensitized to light by depositing an electrical charge uniformly on its surface in darkness. Exposure to a light pattern, either by contact or projection, then reduces the original charge at any point in proportion to the light intensity, thereby forming a latent electrostatic image. Development to yield a visible image is accomplished by various methods of dusting the electrostatic image with charged powder particles. Once formed, the powder image can be used for projection directly from the plate surface, or transferred to another surface for remote projection, or transferred to paper for use as "hard copy." The photoconductor can be cleaned and re-used thousands of times, giving a very low operating cost for consumable supplies. Figure 1 reviews schematically the step-by-step creation of a xerographic image.

Presented at the Rapid Processing Symposium, Washington, D.C., 14 October 1960. Received 16 November 1960; revised 6 February 1961.

1. J. H. Dessauer, G. R. Mott and H. Bogdonoff, *Phot. Eng.*, **6**: 250 (1955).

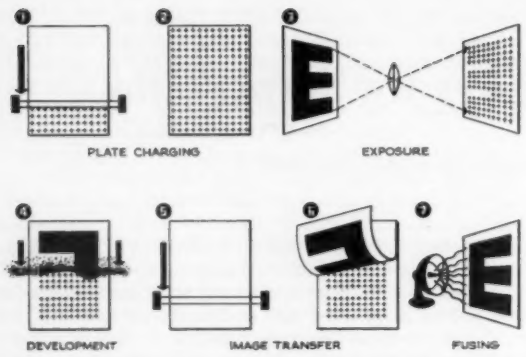

Fig. 1. Schematic representation of the basic xerographic processing steps.

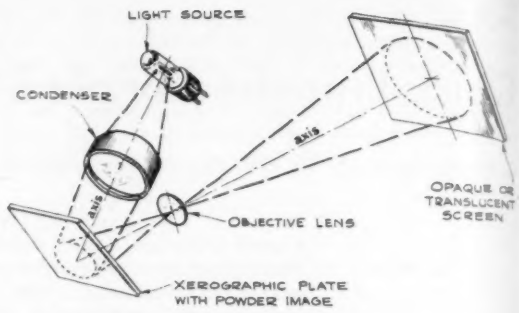

Fig. 2. The PROXI optical system.

Xerographic Processes for Bright Display

PROXI System

A new type of projection system has been devised, called PROXI, a coined name for "Projection by Reflection Optics of Xerographic Images." In this process, a charged xerographic plate is exposed to optical information, then rapidly developed to produce a powder image which is suitable for bright display without the need for further processing of any kind. The speed of xerographic development and the elimination of all extra steps combine to give PROXI techniques simplicity and access times of less than 1 sec.

In addition to very fast access, the displayed information is nonvolatile, i.e., it is not lost in the event of power failure or equipment breakdown. Screen brightness can be very high, as much as 100 ft-L in some cases, in addition to high image contrast and definition. The processed data can be transferred to paper or other supports for permanent storage, if this is desired; otherwise a purely visual display can be produced. Finally, color can be added to the display by several methods.

The Optical System

The PROXI optical system, shown schematically in Fig. 2, makes use of the surface reflectivity of a xerographic plate. A convergent beam of light is produced by the condensing system and, after specular reflection from the plate surface, is brought to a focus at the position of the objective lens. Thus all the light reflected from the plate is collected by the optics. The xerographic plate serves not only as a mirror to "fold" the optical system, but contains a powder image representing the information to be projected. Light scattered and absorbed by the powder is lost from the optical system and thus, when an image of the plate surface is focused on the screen, the powder areas appear as black on white. It is significant to note that this opaque projection system gives a high efficiency more comparable to that of a transparency projector than to the low efficiency of an ordinary opaque projector, despite the fact that the reflectivity of an amorphous selenium plate is only 27%. This difference is a direct consequence of the fact that the light is collected effectively through specular reflection rather than ineffectively through scattering by a nonspecular surface.

Table I summarizes the relative brightness of familiar surfaces seen by opaque projection, using an optical system of the type shown schematically in Fig. 2.

In the test system, the surface sample was illuminated and viewed in directions making an angle of 17° with its normal. The objective was an $f/4.5$ lens, 7-in. focal length, set to produce a magnification of 5 × on the screen. The relative brightnesses were obtained as direct measurements of the screen illumination in each case. The incident light represented a beam of $f/3$, while the detector measured essentially only the normal component of the flux reaching the focal plane.

TABLE I
Relative Brightness of Surfaces

Material	Relative brightness
Polished aluminum	100
Selenium	30.5
Ferrotyped photographic paper (unexposed, flat mounted)	5.0
Semimatte photographic paper (unexposed, flat mounted)	3.0
White bond paper (flat mounted)	2.5

It is significant to observe the great loss of brightness for the nonspecular surfaces.

In addition to giving high brightness, the PROXI system can provide images of excellent contrast. The light scattering and absorbing properties of fine powders in the PROXI system are best illustrated by comparing the photographic densities produced by identical powder images viewed in three different ways: by PROXI from a selenium plate, by transmission through a transparency, and by reflection from an opaque paper surface.

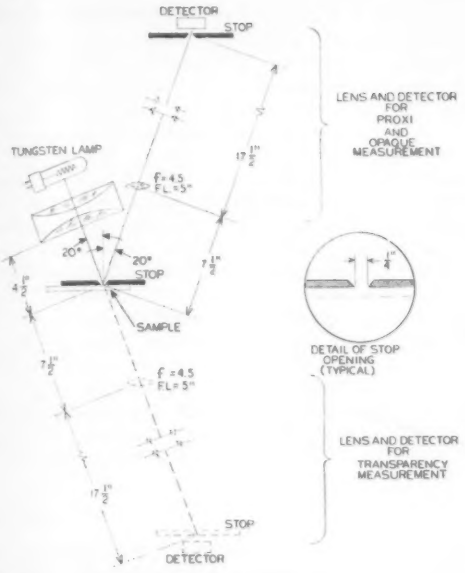

Fig. 3. Optical system for density comparison.

A xerographic plate was exposed to a gray scale and developed by powder cloud methods so that each step contained a different quantity of powder per unit area. This image was then observed in a PROXI system and the brightness ratios measured, thus giving the relative densities of the projected display. Subsequently, the powder from half the plate was completely transferred to a transparency and the other half to gelatin-coated paper. All three samples were measured, using the same optical system as shown in Fig. 3. For the PROXI and opaque samples, the upper configuration, involving reflection, was used; for the transparent sample, the lower "in-line" configuration was used. In each case, the relative densities of the bare selenium plate, the untransferred paper, and the untransferred transparency samples were measured. The results of the test are summarized in Fig. 4 which indicates the superiority of PROXI over both the transparency and the opaque systems.

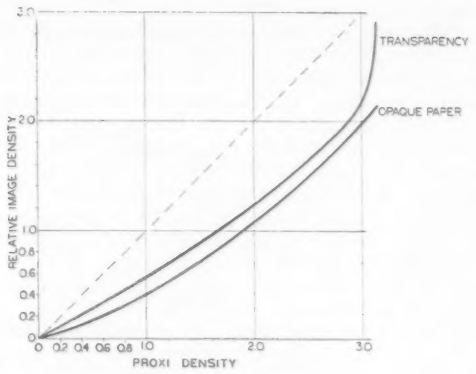

Fig. 4. Powder density vs. observation method.

Types of Display Mechanisms

Depending on the type of information furnished to the xerographic recorder-reproducer system and the processing methods used, the display may consist of black lines and characters on a bright background, bright lines and characters on a dark background, or continuous-tone pictures. Colored lines and characters on a black background may be obtained by adding color filters to the projection system which is displaying the white-on-black information. Several colors can be shown simultaneously by using as many separate projectors as the number of colors desired.

The system can be adapted to produce a bright display of stationary or moving images derived

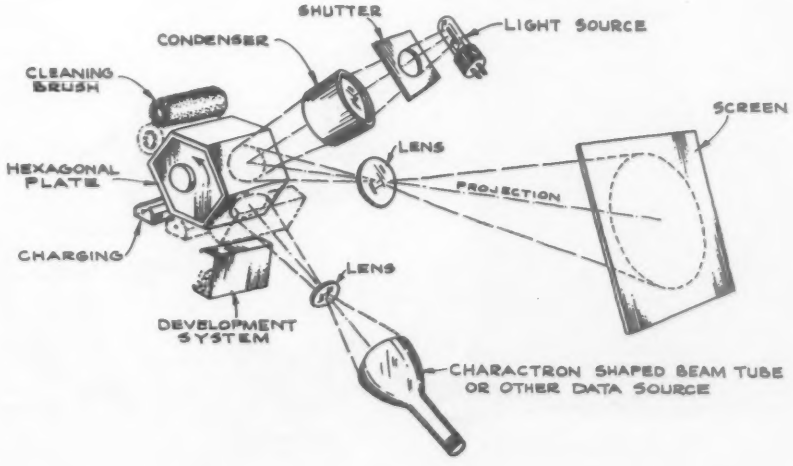

Fig. 5. Intermittent full-frame system.

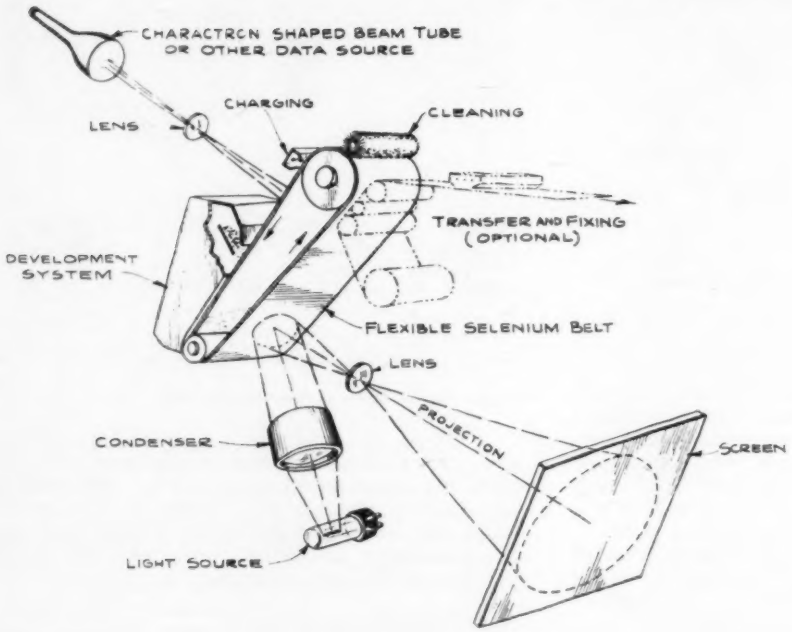

Fig. 6. Continuous projection system.

from optical inputs which are either stationary or moving.

To indicate the variety of PROXI bright display systems which are possible, several representative types are described briefly below.

Intermittent Full-Frame System

Figure 5 suggests a system adapted to record and display a full frame of information such as PPI radar scan, a full-page computer readout, tabular data, a photograph, or a real-life scene, while the plate is stationary. Selenium plates are mounted on the faces of a polygonal "drum" which can be indexed rapidly from one position to the next by a Geneva movement or equivalent mechanism. While stationary, a charging unit sensitizes the lower face; then the "drum" is rotated to the exposure position where the frame of data is "read in" from a cathode-ray tube, optical projector, or camera. When exposure is complete, the image is developed and the "drum" is turned to the projection station, replacing the previously processed image.

After viewing, the image may be transferred to paper for a permanent record. On the next cycle, the residual image is brushed from the plate, preparing it for re-use.

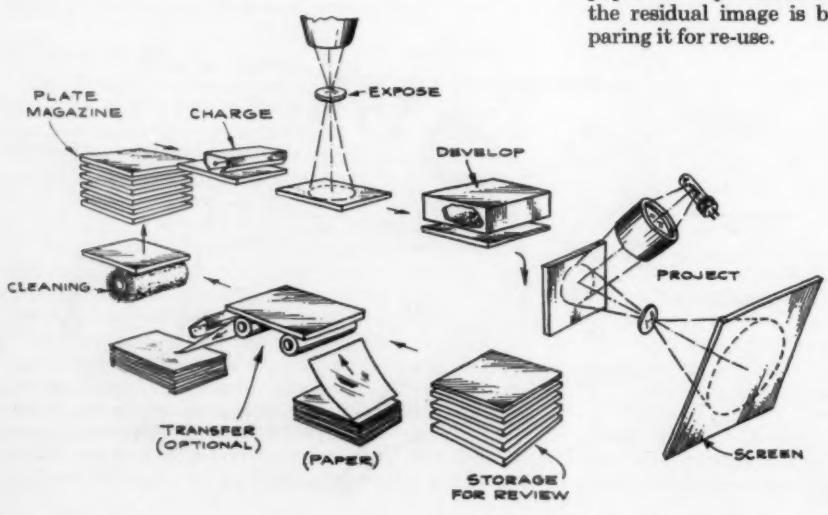

Fig. 7. Magazine system.

Continuous Projection System

The device shown in Fig. 6 is a practical approach to the problem of recording and displaying information being received on a line-by-line basis. This includes teletype, facsimile, side-looking radar, communications monitoring, and others.

The "heart" of the machine is a flexible photoconductor belt prepared by coating selenium onto thin metal or plastic material having a conductive surface. The selenium surface moves continuously past the charging station to the exposure position where a cathode-ray tube or other source "reads in" the information line by line. After development, the image moves across the screen, which is large enough to make many lines visible at a time. The operator reads or interprets the display as it moves, and upon his demand a paper "hard copy" can be prepared for future reference or further study. The cleaning operation prepares the plate for re-use and the process is complete.

Magazine System

The arrangement shown in Fig. 7 permits a greater flexibility in the exposure and viewing conditions than either of the previous systems. Separate flat plates are stored in a magazine and can be handled independently by the mechanism. A plate is first automatically fed out past the charging grid to the exposure station. If a full-frame exposure is to be made, the plate can be stopped in the proper position while the data are "written in" optically. For slit exposure, on the other hand, the plate can be moved across the field continuously. After exposure, the plate is developed and fed to the viewing station for inspection as long as desired. Plates can then be stored for possible review or fed to a transfer station for "hard copy" preparation, and finally on to be cleaned and returned to the magazine.

Applications

The PROXI bright display technique, especially in the form of a direct-view console, is applicable to many types of information-handling systems.

Although commercial applications have not yet been established, several very promising possibilities exist. Some of these have been mentioned in the earlier discussion of display mechanisms, and can be summarized as follows: A full-frame stationary display can be made of data presented on a cathode-ray tube serving as the output of any system such as PPI radar, slow scan TV, closed circuit TV, computer output or facsimile. The PROXI system can also receive optical images from cameras recording documents or real-life scenes. Continuously moving displays can be made of very long or strip-type inputs from side-looking radar, teletype, or facsimile, using a cathode-ray tube to provide the optical image. Applications such as these include reconnaissance, air traffic control, communications, and data storage-retrieval systems.

The PROXI system and its applications, as described, make use of the fact that the developed xerographic plate can serve as the input for a bright display projection system. In addition, and of basic importance, it represents an extremely compact and inexpensive storage of information. Information presented to a xerographic plate by a communication system need be "read in" only once, in contrast with the repetitive scanning of conventional television, then is held in a directly usable form. In multiple distribution systems, particularly those using a central storage facility, this buffering capability will enable wide bandwidth communication channels to be used at high efficiency. Following display, a developed xerographic plate can be stored for a period as long as desired, then removed from storage for review on demand. If long-term storage is necessary, the powder image may be transferred to paper and fixed, giving a permanent "hard copy."

A completely functional PROXI processor-projector has been constructed for study and demonstration purposes. This equipment is shown in Fig. 8. Selenium plates measuring 3 by 3 in. are stored in a magazine, charged, exposed to a simulated cathode-ray-tube presentation, developed, and displayed on demand on the 15 by 15-in. rear projection screen. The access time—i.e., the interval required between the termination of exposure and the beginning of display—is approximately 1.5 sec. The equipment is designed to process only high-contrast line-type input, but could be readily provided with a continuous-tone capability. Screen brightness is approximately 100 ft-L with a 750-w incandescent projection lamp in the optical system. The convenient size of the xerographic plates makes for ease in storage and handling.

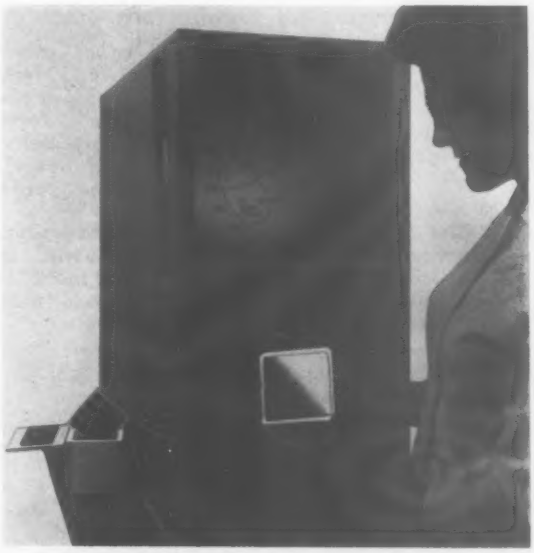

Fig. 8. PROXI processor-projector equipment.

Large Screen Projection

The screen size and brightness for a PROXI display of the type described are limited by the characteristics of the selenium photoconductor. Exposure to high light levels is necessary during the projection step, and although xerographic plates can be manufactured in such a way that their behavior is reproducible from cycle to cycle despite this exposure, there is, nevertheless, an upper limit of exposure which plates can tolerate. In view of these limitations, the PROXI systems which have been described are not suitable for making large-screen bright displays for viewing by large audiences.

However, it is possible to overcome these limitations and permit large-screen displays having size and brightness characteristics limited only by optical systems and light sources. These systems use an additional transfer step for the creation of a transparency for projection in a conventional optical system. Access times are not as short as for the xerographic plate PROXI systems, but the additional time required for the extra transfer step can be of the order of 1 sec, depending on the configuration, giving a bright display with a total access time of about 2 sec.

The powder image formed on the surface of a xerographic plate can be transferred by electrostatic techniques to many types of insulating surfaces, including transparent plastic sheets. Since the operation can be accomplished in a very short time, it is practical to produce a transparency and advance it quickly into the gate of a conventional projection system for large-screen display. Following transfer, the xerographic plate can be brushed to clean the surface, making it ready for re-use; and to reduce the operating costs of such a machine still further, the transparent medium can also be cleaned and re-used.

The transparency large-screen projection system is adaptable to any of the recording and display arrangements described previously, and can be used in any application where the selenium plate PROXI technique is used. Somewhat longer access times and increased mechanical requirements characterize the system in comparison with the selenium plate PROXI method.

Acknowledgments

The authors wish to express their thanks for the assistance and cooperation of members of the Haloid Xerox research staff: E. Lehmann and R. Rogers for optical layouts and design work, and J. Bickmore and B. Norton for optical measurements.

1961 Annual Conference

May 22–26

Arlington Hotel, Binghamton, New York

The 1961 Annual Conference of the Society, to be held the week of May 22 in Binghamton, N.Y., will offer 50 technical papers and a technical exhibit of a wide variety of new instruments. A special panel will discuss "Communication Theory in Photography," and there will be sessions devoted to color, the testing of photographic materials, aerial photography, photogrammetry, and the characteristics of photographic materials. A special feature will be a review of the wet-plate process, to mark the Civil War Centennial. See page 124 for abstracts of the papers now scheduled.

Registration: All those planning to attend are urged to register and make reservations for accommodations early. Conference registration and accommodations reservation cards are being mailed to SPSE members. Others may obtain cards from A. F. Jennings, and every one is requested to return completed cards to:

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Ansco Recording Films and Rapid Processing Techniques

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A cathode-ray tube recording film and a rapid process technique were developed which permit processing in extremely short times. The various applications of such rapid processing systems are discussed in detail.

The rapid advancements in the field of electronics, such as radar and television, have prompted the photographic industry to seriously consider new techniques for rapid processing of photographic films. The need for speed is especially great for military purposes, in particular in airborne rapid processing of films which may be exposed by conventional methods of aerial photography as well as in cathode-ray tube (CRT) recording from radar and infrared sensing devices.

This paper deals essentially with rapid processing in conjunction with CRT recording for airborne use. However, rapid processing of film is not necessarily limited to military uses but may be adapted for industrial and commercial purposes as well.

The term "rapid processing" can be misleading. For example, for years motion-picture processing has been carried out in large processors with a film travel rate of anywhere from 10 ft to 100 ft or more per minute. This could be considered "rapid processing"—at least the film is moving quite fast—but due to the size of the processor, the film is receiving relatively normal processing. Therefore a better term is "rapid access processing," which refers to the time between exposure and viewing of a photographic image. Rapid access of a viewable image is really the end objective—with rapid processing the means to the end.

The Photo-Receptor

In 1956, Ansco initiated a study program for rapid processing of photographic films. A survey of approximately fifty films was made to determine their photographic characteristics and rapid processing capabilities, particularly for recording of blue-emitting CRT phosphor screens such as P-5, P-11, and P-16. It quickly became evident that few, if any, of the then commercially available films could meet the requirements for this type of photography and processing. This survey made possible the determination of characteristics a film needs for this type of photography. These characteristics are:

1. *Photographic Speed:* ASA Exposure Index is of little value in selecting films for CRT recording, since most of the phosphors used are blue-light emitting and do not utilize much of that portion of the spectrum to which orthochromatic and panchromatic films are sensitized.
2. *Contrast:* The limited range of densities reproduced by the recording system, and the primary requirement for obtaining maximum information in the areas of lowest light level, indicates the need for a high contrast negative film. Films with gamma 1.8–2.6 give satisfactory results.
3. *Sensitivity:* The blue-emitting P-5, P-11, and P-16 phosphors offer optimum actinic light level as compared to green or mixed blue-green phosphors. Film emulsions sensitive only to blue light, and matching the peak-emission wavelength of the phosphor, minimize the effect of background glow from the tube filaments and allow film handling in yellow-orange safelights.
4. *Resolution:* The film should give minimum halation and maximum resolution without antihalation backing or screening dyes in the emulsion.
5. *Film Emulsion:* Since most rapid processes of photographic films are dependent on raising the temperatures of the processing solutions, the film emulsion should be stable at temperatures up to 60°C in alkaline developers, able to resist mechanical abrasion, and retain normal photographic characteristics.
6. *Rapid Processing:* The film should, of course, develop and fix in a relatively short time.

With these requirements established, a product called "Hyscan" Recording Film was developed.

Ansco Hyscan Recording Film

Ansco Hyscan is a fine-grain high-resolution highly hardened blue-sensitive photo-recording emulsion,

Presented at the Rapid Processing Symposium, Washington, D.C., 15 October 1960. Received 22 December 1960.

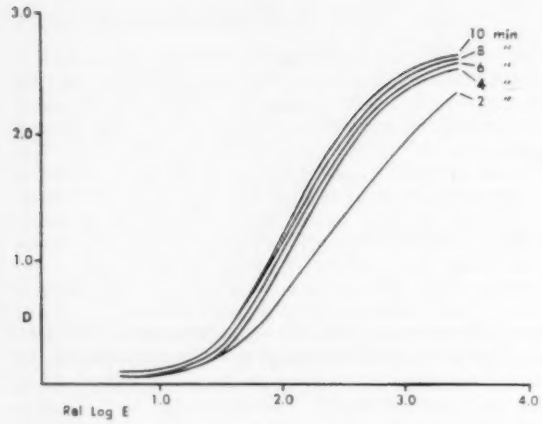

Fig. 1. Normal processing: Ansco Hyscan developed in AFD No. 1 at 20°C.

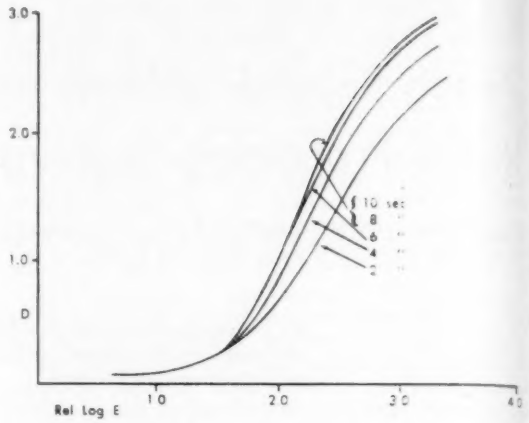

Fig. 2. Rapid processing: Ansco Hyscan developed in Hyscan Rapid Developer No. 300 at 50°C.

coated on clear or yellow-dyed aerial reconnaissance film base. It is designed specifically for airborne rapid processing of blue-emitting phosphor line-scan CRT presentations from side-looking radar systems. However, this film has been successfully field-tested in recording a wide variety of full-screen radarscope presentations, oscilloscope wave forms, digital tube characters, and data instruments, as well as CRT presentations from infrared sensing systems.

Typical characteristics of Ansco Hyscan Recording Film are as follows:

1. *Spectral Sensitivity:*
   a. Tungsten lamp: 350–520 mμ, peak at 460 mμ.
   b. Equal energy distribution light sources—glass optics: 340–520 mμ, peak at 375 mμ.
2. *Resolution:* Maximum high-contrast square-wave photographic resolving power: 100 lines/-mm. Frequency response (square-wave input/-sine-wave output): 110 lines/mm.
3. *Film Speed:* Exposure Index: Daylight, 20; Tungsten, 6. Blue light response equivalent to a panchromatic film with a Daylight Exposure Index of 60.
4. *Emulsion:* Hyscan emulsion is thin but high in silver content per unit area, yielding high density, and hardened to withstand processing temperatures as high as 80°C without excessive swelling and softening.
5. *Normal Processing* (Fig. 1): Ansco Permadol Developer or AFD No. 1: 8 min at 20°C.
6. *Rapid Processing* (Fig. 2): Hyscan Rapid Developer No. 200 or No. 300: Minimum time, 5 sec at 50°C.

A blue-green sensitized film (Hyscan-Ortho) and a panchromatic film (Hyscan-Pan) also were developed.

Processing Techniques

In the field of rapid access processing, we initially investigated one-step diffusion transfer, liquid monobath, viscous monobath, and multistep conventional developing and fixing processes, with the following conclusions:

1. Diffusion transfer processes are slow-acting, requiring an excessive time-delay between exposure and viewing; also, the negative is too low in contrast to be used in making additional prints by conventional means.
2. The liquid monobath process would seem to be ideal, since only one solution is needed, but in practice it has some serious disadvantages for airborne rapid processing. It requires a rela-

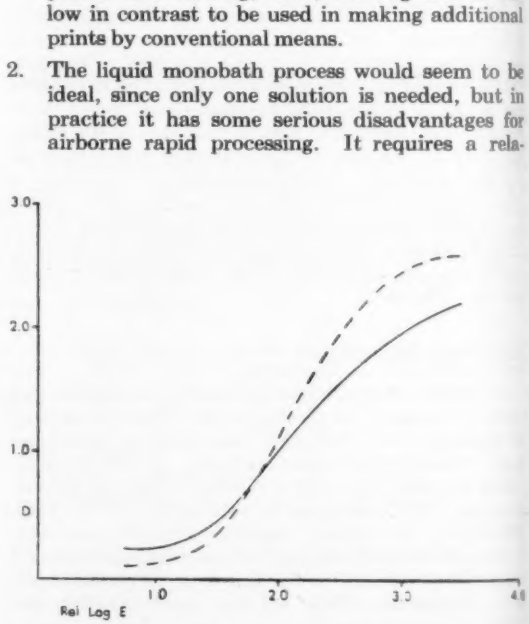

Fig. 3. Rapid monobath processing vs. normal processing: Ansco Hyscan Film. Broken curve—Ansco Permadol Developer, 8 min at 20°C; solid curve—monobath, 20 sec at 50°C.

tively large solution volume, rapidly accumulates silver sludge which in turn presents mechanical problems, often shows short operating life, may give a high fog level, and gives excessively low film contrast (Fig. 3).

3. Viscous monobaths allow a certain saving in solution volume, as they can be applied in a layer as thin as 3.5 mils thick. However, this layer must be removed after use to prevent discoloration of the film and to prevent extrusion of the residue material when the film is wound. Even the insertion of an interleaving protective foil is not very satisfactory. In addition, the uniform application of viscous layers across a wide moving film strip requires precise, complex applicators, uneconomical in space and weight.
4. Conventional photographic development, followed by fixation, offers normal optimum photographic quality but requires excessive solution quantities as well as wash water. Changes in processing rates, for instance, resulting from changes in ground speed of an aircarft (reflected as a change in rate of film travel), require immediate compensation by means of temperature or by mechanically varying the length of the film path through the processing solutions.

In reviewing these various approaches to rapid processing of film, it was felt that the best approach was the conventional multistep process, because of the near optimum results obtained, repeatability, and reliability of the process. However, the indicated disadvantages of conventional processing had to be overcome.

Arrested Development Technique

The photographic objective of Ansco's first airborne rapid processing system was to view a photographic image, in the shortest possible time, after the film was exposed to a CRT presentation. It was found possible to view an unfixed film emulsion on a backlighted viewer immediately after it had been developed and stop bathed, without an undue increase in fog density resulting from continued reduction of the residual halides. Toward this end, a developer that develops Hyscan film in a minimum time of 5 sec at 50°C and a post-bath solution which sufficiently stabilizes the unfixed negative in 1 sec at 50°C for viewing on a white backlighted panel were formulated. This processing became known as Ansco "arrested development rapid processing technique."

The developer solution, Hyscan Rapid Developer (HRD) No. 300, is highly concentrated and has a pH of 12.8. Organic additives are used to inhibit development fog and to help stabilize the residual halide to light. These restrainers also tend to limit over-development once optimum development has been achieved, thus allowing the film to remain in the developer 10 to 12 times longer than the minimum development time of 5 sec (Fig. 4).

The post-bath neutralizes the alkaline developer and rinses the film of any developer remaining on the emulsion.

These solutions also have extremely high processing capacity. One liter of HRD No. 300 will process 100 ft of 9 $^1/_2$-in. (11,000 sq in.) Hyscan Recording Film with little change in effective energy level, and only 0.5 liter of post-bath is required for this amount of film (Fig. 5).

The developer has a useful solution life of at least 24 hr at 55°C in a rapid processing system and approximately 6 months at 20°C in full well-stoppered bottles. The shelf life of the post-bath is indefinite.

System Processing Technique

The Ansco rapid processing technique involves passing the film emulsion over a small slotted cham-

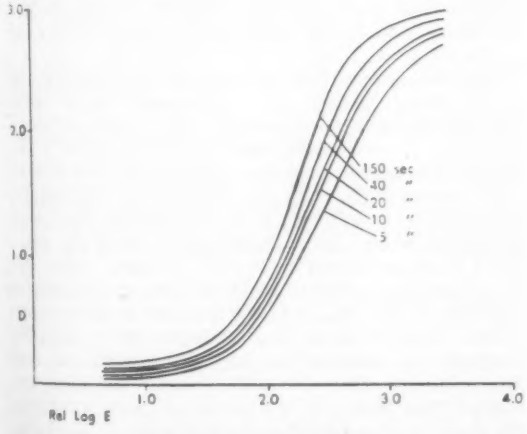

Fig. 4. Effect of varying developing time: Ansco Hyscan in "arrested development" (HRD No. 300) at 50°C, fixed prior to viewing.

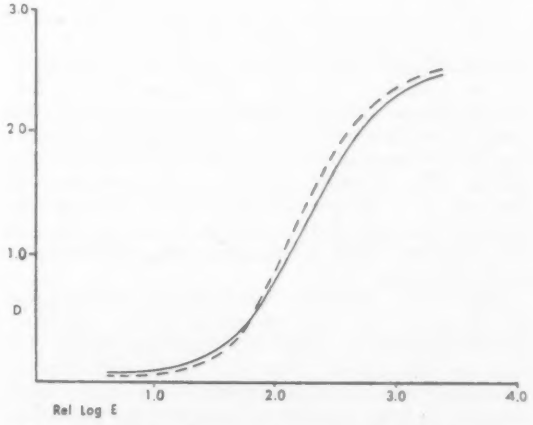

Fig. 5. "Arrested development" exhaustion characteristics: Ansco Hyscan, 5 sec at 50°C, fixed prior to viewing. Solid curve—fresh solution; broken curve—exhausted by 100 ft of 9 $^1/_2$-in. film per liter developer.

ber in which hot developer is circulating under negative pressure. The chamber is designed in such a way that the developer penetrates the thin emulsion completely and uniformly. As the film leaves the chamber, the exit edge of the slot presses against the film, thus acting as an efficient squeegee. Due to the low swelling characteristics of the film, and the relatively low coating thickness, the amount of developer remaining on the emulsion is minute. The film then moves over a narrow slot where the emulsion is treated with the post-bath solution.

The damp negative may be viewed in white light within seconds. The film surface is dry at the point of windup, and the film may be rolled up without danger of emulsion damage, making an auxiliary foil separator unnecessary.

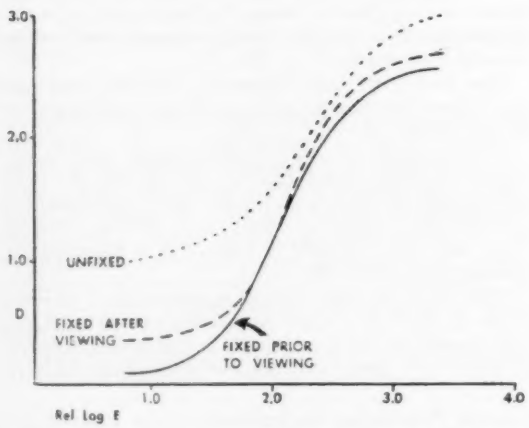

Fig. 6. "Arrested development": Ansco Hyscan, 5 sec at 50°C.

The Processed Negative

Typical characteristics of a negative processed by the "arrested development" technique (Fig. 6) are as follows: The unfixed negative, as presented on the viewing panel, has a minimum density level which approximates 0.8 density and a gamma of 1.5. After viewing and subsequent fixing, the ultimate fog level approximates 0.2 density and the gamma is 2.0. The "arrested development" processed film can remain in the unfixed state for over a year with no deterioration of film quality, and may be fixed and washed at any convenient time, producing an archival transparency.

The Ansco Systems Development Department has designed and built advanced camera-processor-viewer systems to utilize this rapid processing concept to the fullest (Fig. 7). A typical camera-processor-viewer system consists of two main units, the camera body and the processor-viewer assembly.

The camera body contains an optical system for imaging a CRT line scan onto the film. Also, a data box usually is incorporated into the camera body to record time, date, etc., on the film.

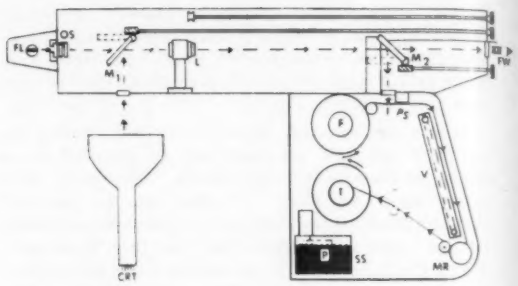

Fig. 7. Schematic diagram of an Ansco camera-processor-viewer for CRT line-scan presentation.

CRT—Cathode-ray tube
FL—Fluorescent light
OS—Optical slit
M_1, M_2—Mirrors
L—Lens
FW—Focusing window
I—Imaging on film at focal plane
F—Film supply
PS—Processing station
V—Viewer
MR—Metering roller
T—Take-up
P—Pumps (in solution tanks)
SS—Solution supply

The processor-viewer unit contains the film supply and take-up, processing station, viewer, processing solution tanks, drive motors, and gear assemblies. The processing solution tanks have built-in pumps, heaters, and thermostats which control the temperatures and flow of the solutions to the processing station.

The power supply and control panel may either be a third unit or integrated into the camera and/or processor-viewer assemblies.

Expanding the "Arrested Development" Technique

The "arrested development" technique has one disadvantage, the retention of the residual halide on the film. So as not to limit ourselves only to rapid viewing of a backlighted image, techniques were devised for clearing the remaining silver halide on the film to obtain a negative of normal process quality.

High concentrations of sodium and ammonium thiocyanates having low exhaustion rates clear Hyscan film in approximately 1 to 1.5 sec at 50°C. One liter is capable of clearing 100 ft of 9 $^1/_7$-in. film under normal exposure conditions. However, the concentrated thiocyanates attack the gelatin in the photographic emulsion, making the film emulsion hygroscopic, and a slight tackiness of the processed emulsion seems to be ever present. Also, the processed film is very unstable to heat and humidity, resulting in staining and fading of the image in 24 to 72 hr. Some of these disadvantages can be partially overcome by treating the film with a chemical rinse immediately after the thiocyanate solution has cleared the film. If conventional post-processing by fixing and washing is done within 48 to 72 hr after the initial rapid process, archival quality can be achieved.

However, since the above-described clearing systems could not meet all the desired qualifications for an optimum rapid processing system, other approaches were investigated.

A rapid clear-stabilization system finally was formulated which provides optimum film quality under rapid processing requirements and conditions. This latest technique requires the use of two solutions: a solution that clears the remaining silver halide in the developed film in 1.5 to 2.0 sec at 50°C and a 1.0-sec chemical rinse at 50°C that stabilizes the photographic image. It is estimated that under normal storage conditions, the rapid processed film thus cleared, without any further post-processing, will remain usable for at least two years. These solutions have low exhaustion rates; 1 liter of each solution is sufficient to clear and stabilize 100 ft of 9 1/2-in. normally exposed and developed Hyscan-type film.

Using the Hyscan Rapid Developers in conjunction with this rapid clear-stabilization technique, Hyscan Film can be processed in a total time of 7.5 to 8.0 sec to obtain normal-process film quality.

Rapid Reversal Processes

Hyscan film can also be used for black-and-white reversal processing. Two methods of reversal processing are of interest: (1) a full rapid reversal process which can be completed in approximately 30 sec at 50°C, and (2) a rapid three-step partial reversal process, using only three solutions.

The partial reversal process consists of developing the film, bleaching the developed silver, and chemically rinsing to clear the highlight areas of yellow bleach-stain. The remaining silver halide in the film yields good contrast and detail when this image is projected onto a screen. On an experimental basis, this partial reversal process has been carried out in a total chemical processing time of 5.0 to 7.5 sec at temperatures of approximately 70°C, using a high-contrast experimental Hyscan-type film.

Conclusion

The combination of film, processing solutions, and a rapid processing technique has resulted in building camera-processor-viewer systems that permit viewing of a photographic image 8 sec after exposure. The rapid process film quality obtained compares to normal-process film quality and retains this quality, under normal storage conditions, for approximately two years.

• Coming Technical and Scientific Meetings

89th Semiannual Convention, Society of Motion Picture and Television Engineers, May 7–12, King Edward Sheraton, Toronto, Ont.

American Rocket Society, National Telemetering Conference, May 22–24, Chicago, Ill.

1961 Annual Conference, SPSE, May 22–26, Binghamton, N.Y. To register, write A. F. Jennings, 32 Castle Creek Rd., Binghamton, N.Y.

International Conference on Spectroscopy, June 5–10, Lyons, France

Technical Association of Graphic Arts (TAGA), June 12–14, Deshler-Hilton, Columbus, Ohio

Joint Automatic Control Conference, American Institute of Chemical Engineers, American Institute of Electrical Engineers, American Society of Mechanical Engineers, Institute of Radio Engineers, Instrumentation Society of America, June 28–30, University of Colorado, Boulder, Colo.

International Union of Pure and Applied Physics, International Commission for Optics, July 5–8, Paris, France

International Optical Congress, July 5–10, London, England

Color Photographic Association of Canada, July 9–11, Sheraton-Connaught Hotel, Hamilton, Ont.

International Conference on Optical Instruments and Techniques, July 10–14, London, England

National Audio-Visual Association, Annual Convention July 22–25, Hotel Morrison, Chicago, Ill.

Professional Photographers of America, Annual Exposition of Professional Photography, July 30–August 4, Statler-Hilton, New York

American Rocket Society, Guidance and Control Conference, August 7–9, Stanford University, Stanford, Calif.

Society of Photographic Instrumentation Engineers, Annual Technical Symposium, August 7–11, Ambassador Hotel, Los Angeles, Calif.

Biological Photographic Association, Inc., August 21–24, Chicago, Ill.

International Conference on Photoconductivity, August 21–24, Cornell University, Ithaca, N.Y.

Electron Microscopy Society, August 25–September 5, Philadelphia, Pa.

International Congress of Radiology, August 26–September 1, Montreal, Que.

American Chemical Society, 6th International Conference on Coordination Chemistry, August 27–September 1, Wayne State University, Detroit, Mich.

Inter-American Congress of Radiology, September 3–10, Saõ Paulo, Brazil

(*Continued on page 114*)

PHOTOGRAPHIC SCIENCE AND ENGINEERING
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New Photographic Processes

I. The Arylamine-Carbon Tetrabromide System Giving Print-Out Dye Images

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A new photosystem utilizes free radicals generated from polyhalogen compounds by near ultraviolet irradiation and their reaction with arylamines to form a direct print-out dye image. The mechanism of the dye-forming reaction is discussed, and the procedure for isolation and identification of the blue dye of which the image is formed is described. Speeds twenty times faster than diazo have been obtained, and there are indications that much greater speeds are possible.

It is well known that polyhalogen compounds, such as carbon tetrachloride, carbon tetrabromide, and the like, are split into free-radical fragments on irradiation with ultraviolet light.[1] Use of this reaction is made in photopolymerization processes, where the free radicals thus formed initiate a chain reaction resulting in the production of polymers of high molecular weight.[2] Carbon tetrabromide has also been used to introduce bromine atoms into other organic compounds under the influence of ultraviolet light.[3]

In the course of a study of various polymerization initiators, E. Wainer observed that near-visible ultraviolet irradiation of a mixture of CBr_4 and diphenylamine in benzene solution gave an intense blue coloration, and it occurred to him that this color formation might be used as the basis for a new photographic process. Other secondary and tertiary arylamines were also found to give colors with polyhalogen compounds, and a systematic investigation of such photosystems was undertaken.

The problem was attacked on two fronts, one being the elucidation of the reaction mechanism by which the colored image was formed and the determination of its chemical composition, and the other designed to explore the utility of the process in photographic applications. Although different arylamines gave somewhat different colors in the process, it was suspected from the start that the mechanism of reaction was the same in all cases, and the dyes therefore probably all belonged to one class.

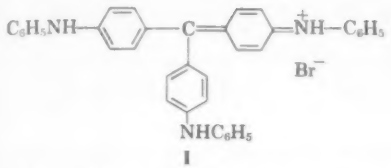
Presented at the Rapid Processing Symposium, Washington, D.C., 15 October 1960. Received 21 November; revised 30 December 1960.

1. M. S. Kharasch, *J. Am. Chem. Soc.*, **68**: 155 (1946).
2. M. S. Kharasch, et al., *J. Am. Chem. Soc.*, **69**: 1100 (1947).
3. E. Huyser, *J. Am. Chem. Soc.*, **82**: 391 (1960).

Isolation and Identification of Dye

The diphenylamine–carbon tetrabromide reaction was selected for experiments aimed at isolating a sample of pure dye, because it gave unusually rapid color formation, and the intensity of color promised a relatively good yield. It was found that the dye could be prepared most readily by exposing to ultraviolet light sheets of filter paper impregnated with an acetone solution containing diphenylamine and carbon tetrabromide. Unchanged carbon tetrabromide and diphenylamine were removed by extracting the papers with hot benzene, and the dye was isolated by subsequent extraction with methanol. On evaporation of the alcohol solution to small volume and chilling, the dye crystallized, and it was purified by recrystallization from methanol. The usual tests showed that the product was a basic dye, probably of the triphenylmethane series. It was reversibly decolorized by alkali, the color returning on acidification; it was reduced to a colorless leuco form by sodium hydrosulfite or zinc and acetic acid; the leuco compound could be reoxidized to the dye by oxidizing agents but not by atmospheric oxygen; the dye contained the bromide ion and was therefore a salt, which was in agreement with the observed high melting point (above 340°C). Spectrophotometric curves were run, and the dye was found to have a very sharp maximum at 585 mμ in methanol solution.

It seemed probable that, if carbon tetrabromide had reacted with diphenylamine to form a triphenylmethane dye, the function of the halogen compound would be to provide the bridge carbon atom linking the three phenyl groups. Condensation of CBr_4 with three molecules of diphenylamine at the relatively active para position to the nitrogen, with the elimination of hydrogen bromide, would give dye **I**.

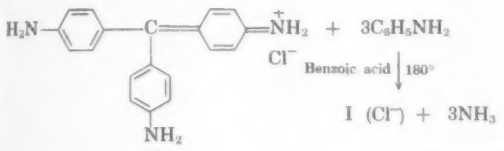


I

The elemental analysis of the dye was in fair agreement with this structure. *Anal.* Calc'd. for $C_{37}H_{30}BrN_3$: C, 74.50; H, 5.03; Br, 13.35; N, 7.05. Found: C, 73.48; H, 5.19; Br, 12.61; N, 6.68.

According to the *Colour Index*, a dye corresponding to this structure is available commercially from W. S. Simpson and Co., London, England, under the name of *Opal Blue SS*.[4] A sample was obtained and was found to be very similar to the dye isolated from the photoprocess, except that the absorption maximum of the *Opal Blue SS* was at 575 mμ and was somewhat less sharp.

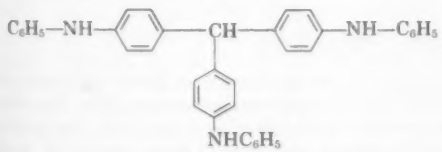
The *Colour Index* also states that treatment of Pararosaniline hydrochloride with aniline and benzoic acid at 180°C. results in the introduction of three phenyl groups, as shown in **II**.[5]



II

This synthesis was carried out in our laboratory, and a blue dye was obtained which, after conversion to the bromide, was identical in all respects with the dye isolated from the photoprocess. The absorption maximum in methanol solution was 585 mμ, and the infrared absorption curves were identical. *Anal.* Found: C, 74.15; H. 5.43; Br, 12.70; N, 7.37.

As a further proof of structure, the three samples of dye derived from the diphenylamine-CBr_4 irradiation, the commercial dye (*Opal Blue SS*) and the aniline Pararosaniline reaction were reduced with zinc dust and acetic acid to the colorless leuco compound. Identical products were obtained, as shown by mixed melting-point determination (168–170°C, with no depression), ultraviolet absorption curves (max, 292 mμ) and identical infrared absorption curves. The elemental analysis agreed with the structure shown below.



p, p,′ p″—Trianilinotriphenylmethane

III

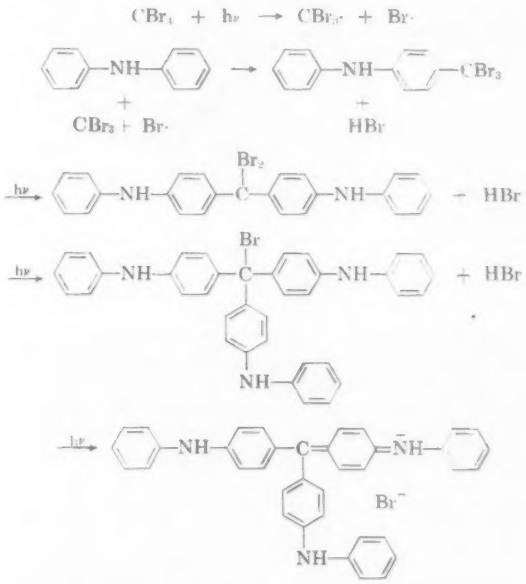
4. *Colour Index*, 2nd ed., Vol. 2, p. 2879.
5. *Ibid.*, Vol. 3, p. 3367.

Anal. Calc'd for $C_{37}H_{31}N_3$: C, 85.82; H, 6.04; N, 8.12. Found (for *Opal Blue SS* reduction product): C, 85.55; H, 6.26; N, 8.19.

The effect of ultraviolet light on a mixture of carbon tetrabromide and diphenylamine has thus resulted in formation of a blue triphenylmethane dye.

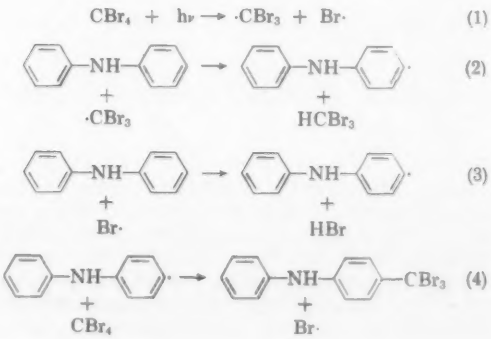
Speculations on the Reaction Mechanism

The mechanism of reaction may be postulated to follow the course outlined below.

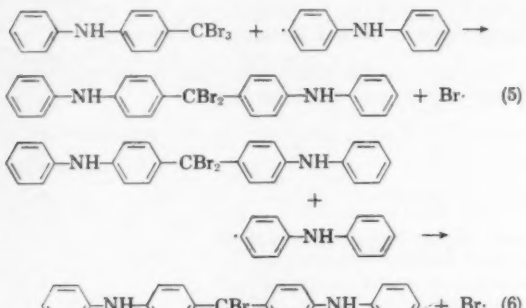


However, the relatively high photographic speeds obtainable with this system (considerably faster than diazo) would seem to indicate that some other mechanism, not requiring four quanta of light for formation of one molecule of dye, is operating here.

A theoretical mechanism for such a chain reaction involves initial formation of active radicals from diphenylamine, followed by condensation of these with CBr_4, as follows:



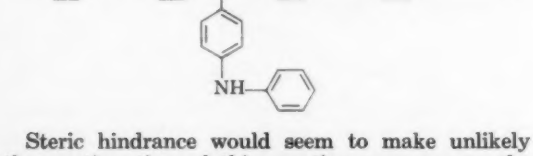
The bromine atom resulting from Reaction (4) might then react with another molecule of diphenylamine, as in Reaction (3), thus assuring a continuing supply of diphenylamine radicals for further condensation. These may react with the product from Reaction (4) as follows:



(5)

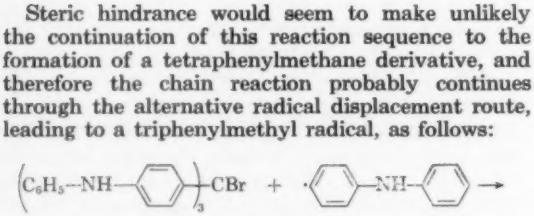
(6)

Steric hindrance would seem to make unlikely the continuation of this reaction sequence to the formation of a tetraphenylmethane derivative, and therefore the chain reaction probably continues through the alternative radical displacement route, leading to a triphenylmethyl radical, as follows:



(7)

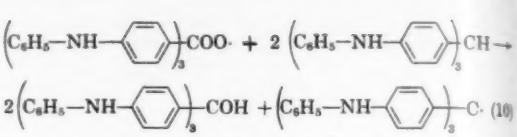
The trianilinotriphenylmethyl radical formed in Reaction 7 may then react with a molecule of diphenylamine, giving trianilinotriphenylmethane and a diphenylamine radical, as shown in Reaction 8, or it may react with atmospheric oxygen to form the peroxy radical shown in Reaction 9:



(8)

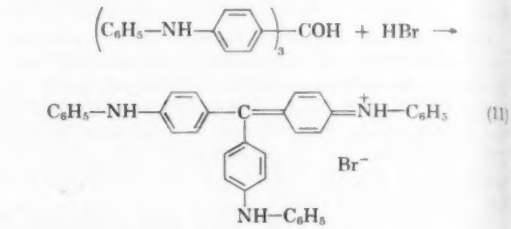
(9)

Peroxy radicals of the type of the product from Reaction 9 are known to be very active oxidizing agents, and in this system may react with the product from Reaction 8, giving the carbinol of the triphenylmethane dye shown in Reaction 10 and at the same time regenerating the trianilinotriphenylmethyl radical needed to carry on the chain reaction:



(10)

The carbinol (Reaction 10) will be immediately converted to the deeply colored form of the triphenylmethane dye by the HBr which is present in the mixture from earlier steps in the chain reaction sequence:



(11)

These preliminary speculations concerning the reaction mechanism of the dye-forming system give some support for the presence of a chain reaction which might make possible relatively high photographic speeds. Many other radical combinations may operate as competing or terminating reactions, and it is therefore remarkable that the dye-forming condensation proceeds in such high yield and with relatively few by-products. A trace of magenta dye is found along with the blue dye, and we plan to isolate and identify this also.

Development of Photographic Process

In the second phase of this study, aimed at development of useful photographic materials based on the arylamine-carbon tetrabromide reaction, several variables were examined. These were: substitution of a variety of amines for diphenylamine, other halogen-containing compounds for carbon tetrabromide, trial of many different binder systems, and attempts to develop fixing techniques to stabilize the image after exposure. In general, the photosensitive compositions were prepared by mixing a solution of the arylamine with a solution of a halogen-containing compound, adding the mixture to a suitable binder solution, such as polystyrene in benzene, and coating the mixture on a substrate.

Coating Procedure

Coatings were made on a Bird vacuum plate. This consists of a hollow aluminum plate, the surface of which has a number of holes, the main hollow chamber being connected to a vacuum source. The vacuum holds the sheet flat while the coating is applied. The applicator bars act as doctor blades and are so machined as to allow only a uniform opening between the blade surface and the surface to which the coating is applied. This opening is

the wet thickness of coating, usually 0.0015 or 0.003 in.

The support used in most of these tests was white opaque polyvinyl chloride film, 10 mil in thickness.

The coated materials were exposed through a negative to the ultraviolet light from a 275-w General Electric sunlamp at a distance of 10 in. Exposures of from 1 to 10 sec gave blue images of good density, depending upon the arylamine used.

Comparative Photographic Speed

Photographic speed can presently be applied with accuracy only to silver halide systems exposed to visible light, followed by standardized wet development. Fundamentally, photographic speed, even though determined by the present rigid and arbitrary method, is more or less directly related to the light flux striking the sensitive surface. It would appear that this fundamental parameter, expressed in such figures as quanta per square centimeter per second, might be utilized for evaluating nonconventional systems.

As a means for establishing the possibilities of developing high speed from a nonconventional system, quantum yield is probably the most important parameter. However, in view of the complexity of the chemical reaction which may take place, it is often not possible to determine the quantum yield with any degree of exactness, since it involves determination of the precise nature of the original light-sensitive material, or complex, and also that of the end chemical which produces the visual result. Once these are determined, then quantum-yield figures can be established with reasonable exactitude, providing the optical characteristics of the end member as a function of its concentration can also be established with certainty.

Though determination of the quantum yield of a nonconventional photographic system is of ultimate value for research purposes, in the last analysis the practical utility is a function of the comparative behavior of such systems in relationship to well known silver halide systems. Consequently, comparative figures utilizing standardized silver halide systems as a basis for comparison represent, possibly, the best means for obtaining data which are at once scientific and also of practical import. Even such a comparison technique must be used with care. The peak spectral sensitivities of both the silver and the nonconventional photographic systems must be roughly about the same wavelength. At the same time, means must be provided for eliminating the variable imposed by the variations in sensitometric response of the systems being compared. For initial screening purposes, therefore, the amount of light required to produce a barely detectable image fulfills such a requirement. It may be argued that such a choice may represent a drastic modification of the actual speed available from a silver halide film. However, if the type of film used for such comparison purposes exhibits a relatively high gamma in its H&D curve, then this objection is overcome. Consequently, only a high-contrast type of silver halide film, such as lithofilm, should be used for the purpose.

The photographic standard utilized as a basis for comparison was the Eastman Kodak Kodalith Ortho Type-2 film having an ASA arc-exposure index of 8 and a tungsten index of 5. Two silver halide papers of standard manufacture were used as comparison devices relative to the Kodalith sheet film. These are the No. 2 bromide enlarging paper and the F-2 contact print paper, manufactured by Haloid Xerox. A Bausch & Lomb grating monochromator with a certified precision grating was employed as the calibrated light source. The grating with which this monochromator is equipped has a focal length of 250 mm, a dispersion in the first order of 66 A/mm and an aperture ratio equivalent to $f/4.4$. The light source is a ribbon tungsten filament enclosed in a thin glass envelope. Though designed initially for work in the visible, useful transmission of ultraviolet down to 3000 A is available from such a lamp. Both the light source and the emission ports are fitted with precision Vernier slits, and neither the entering light nor the exit light is collimated.

The usual exposure conditions in our experiments involved a light-source slit width of 5 mm and an exit slit width of 5 mm. The amount of light impinging on the image plane is directly proportional to the product of the two slit widths.

The monochromator was calibrated by placing an Eppley Laboratories bismuth silver thermopile in the monochromator image plane and measuring the thermopile output with a Leeds and Northrup K-2 potentiometer. At 4000 A and above, a clear glass filter eliminates second-order ultraviolet, while above 6000 A a yellow filter is inserted which eliminates the second-order blue.

A recent calibration for the instrument as described, using a light-source slit width of 5 mm and an exit slit width of 5 mm is given in Table I.

TABLE I. Calibration Table

Bausch & Lomb Monochromator — light-source slit width, 5 mm; exit slit width, 5 mm

Wavelength, A	Energy		Quantum flux, sq cm/sec
	ergs/sq cm/sec	μw/sq cm	
6000	4000	400	13.5×10^{14}
5500	3500	350	10.0×10^{14}
5000	2400	240	6.0×10^{14}
4500	1500	150	3.3×10^{14}
4000	600	60	1.20×10^{14}
3500	250	25	0.45×10^{14}
3000	180	18	0.30×10^{14}

Table II gives some representative data which have been obtained on a variety of photographic systems. At a setting of 3900 A and a 5-mm slit width, the spectral range from 3730 A to 4076 A is covered. Peak sensitivity with the diphenylamine-

TABLE II. Comparative Sensitivities of Photographic Systems at 4000 A

Emulsion	Exposure mm	Exposure sec	Relative (ASA) arc index
Kodalith Ortho Type 2	2	$^1/_{150}$	8.0
No. 2 Bromide Enlarging Paper (Haloid)	1	$^1/_{150}$	16.0
F-2 Contact Print Paper (Haloid)	5	0.1	0.2
K and E Helioz Paper (Diazo)	5	600	0.00003
Diphenylamine-CBr_4-polyvinylchloride	5	30	0.0006
Diphenylamine-CBr_4-nitrocellulose	5	2	0.01

carbon tetrabromide system was found to be in this range.

The reason for the observed high sensitivity at these relatively long wavelengths appears to be formation of a complex between diphenylamine and carbon tetrabromide, which absorbs strongly between 390 and 400 mμ. This complex formation was indicated by the shift in absorption to longer wavelength when relatively concentrated solutions of the two components were mixed. Thus, equal parts of a solution of CBr_4, which gave a density of 0.17 at 338 mμ, and a solution of diphenylamine, which showed a density of 0.30 at 338 mμ, were mixed. The resulting solution gave a density of 1.0 at 338 mμ and a density of 0.17 at 400 mμ, indicating complex formation. The complex appears to dissociate on diluting the solution, as evidenced by a drop in density to 0.03 at 338 mμ when the solution was diluted to one-sixth the concentration of the original mixture.

Continuous-tone prints of excellent quality may be made with these materials. The contrast is roughly equivalent to that obtained with a silver halide contact printing paper, such as Eastman Kodak Azo No. 2, when the latter is developed in the usual way. Since the image is composed of dye molecules rather than aggregates of particles (as with the developed silver image), very high resolution is possible.

TABLE III. Effect of Substitution of Various Amines for Diphenylamine

Amine	Color of image	Speed
p-Aminodiphenylamine	Yellow	Less than diphenylamine
p-Aminophenol	Bluish-gray	Less than diphenylamine
N-Methyldiphenylamine	Blue	Speed near diphenylamine
m-Anilinophenol	Blue-gray	Speed near diphenylamine
p-Phenylazodiphenylamine	Faint yellow	Speed very poor
Di-*p*-tolylamine	Pink	Speed about $^1/_3$ of diphenylamine
Carbazole	Blue-gray	Less than diphenylamine
N,N-Dimethylaniline	Green	Speed near diphenylamine
N,N-Dimethylaniline hydrochloride	No color	None
N-*n*-Butylaniline	No color	None
2-Anilinoethanol	No color	None
N-Phenylglycine	Yellow	Extremely slow
N-Phenylglycine ethyl ester	Yellow	Extremely slow
Triphenylamine	Green	Much less than diphenylamine

Effect of Varying Amine Component

Aromatic amines other than diphenylamine were tried with carbon tetrabromide, in an effort to achieve greater speed from the system and possibly obtain a neutral color instead of the blue. Table III summarizes these tests.

Diphenylamine remains the best aromatic amine found so far for speed and intensity of color.

Effect of Varying Halo Compound

Table IV lists halogen compounds that were substituted for carbon tetrabromide in the diphenylamine combination in attempts to achieve increased speed. These halogen compounds were tried alone and in combinations, but no appreciable speed changes resulted. Many of the compounds of Table IV were tried in combination with carbon tetrabromide.

TABLE IV. Effect of Various Halogenated Compounds in Print-Out System

Halogen compound	Color of image	Speed
Bromotrichloromethane	Violet	About $^1/_2$ of CBr_4
1,3-Dichloropropane	No color	None
Tetrachloroethylene	No color	None
Dibromoethane	No color	None
Tetrachloroethane	No color	None
Carbon tetraiodide	Brown	Less than CBr_4
Hexachloroethane	Blue	Slower than CBr_4
Benzotrichloride	Gray	Slower than CBr_4
p-Nitrobenzotribromide	Green	Close to CBr_4 (unstable)
Hexachlorobenzene	No color	None
Tetrachlorotetrahydronaphthalene	Faint green	Slow
Iodoform	Yellow-brown	Slower than CBr_4
Benzotribromide	Green	Slower than CBr_4

The most significant improvement resulted with the use of hexachloroethane in combination with carbon tetrabromide.

Film Formers

Choice of film-forming binder plays an important role in evaluating reactants. Tetrachlorotetrahydronaphthalene and diphenylamine, when coated with polyvinyl chloride in tetrahydrofuran, gave no visible reaction at all, but when coated from nitrocellulose in methanol solution gave a faint green color with low speed.

In most of the early tests in this investigation, half-second nitrocellulose in acetone was used as the binder. Good speeds were realized with equal-molar proportions of carbon tetrabromide and diphenylamine in the acetone-nitrocellulose coatings, but greater speed resulted when the nitrocellulose was coated from methanol. Diphenylamine-carbon tetrabromide mixes in Saran (polyvinylidene chloride) gave speeds about as fast as with methanolic nitrocellulose, but the sensitivity was retained longer in the Saran coatings. Likewise, Shawinigan Resin D-381 (partially hydrolyzed polyvinyl acetate) in methanol with carbon tetrabromide and diphenylamine gave discernible images with 1-sec exposure to ultraviolet light (G-E Sunlamp), indicating some improvement with this binder.

Addition of waxes to the polystyrene system gave improved speed. Thus eicosane (a straight-chain paraffin hydrocarbon with the formula CH_3-$(CH_2)_{18}CH_3$), when added to this binder system containing diphenylamine, carbon tetrabromide, and hexachloroethane, according to the following formula, gave usable images of good density and definition in 2-sec exposure, through a negative, to the ultraviolet light of a 275-w G-E Sunlamp at a distance of 10 in.:

1 cc eicosane (25% in benzene)
19 cc polystyrene (10% in benzene)
2.4 grams diphenylamine
2.8 grams carbon tetrabromide
0.6 gram hexachloroethane

A comparable formula, using nitrocellulose in methanol, required about 5 sec for the same image density.

Samples of the diphenylamine-carbon tetrabromide system in both nitrocellulose and Saran binders have retained speed and sensitivity through months (four) of room-temperature storage with very little tendency to fog.

Fixing Technique

Stabilization of the exposed image was achieved in two ways, both involving removal of the volatile carbon tetrabromide sensitizer. Exposure of the sheet to a current of warm air in subdued light for a time or short heating under an infrared lamp destroyed residual sensitivity when paper was the substrate. However, solvent extraction with benzene or ethyl acetate was preferable for film coatings. For most purposes, permanence of the image to room lighting is satisfactory. However, since triphenylmethane dyes are somewhat unstable, in some cases it may be desirable to bathe the print in phosphotungstic acid solution, which converts the dye to a more stable salt with improved light fastness.

Summary

A new photographic system has been described, consisting of a photosensitive mixture containing secondary or tertiary arylamines, a polyhalogen organic sensitizing agent, and a suitable binder solution coated on a substrate. This material may be used to produce direct print-out dye images when exposed under a negative to ultraviolet light. Fixing may be accomplished either by heating to drive off the volatile sensitizer or by solvent extraction. Photographic speeds much faster than diazo have been obtained with this system.

Acknowledgments

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High-Speed Direct-Recording Papers

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Silver halide emulsions for the direct recording of oscillograph traces represent a new development in the photographic industry. These emulsions will form an immediately visible image at writing speeds up to 10 in./sec when a super-high-pressure mercury arc is used as the light source. With the same source a latent image is formed at writing speeds up to at least 40,000 in./sec. Such latent images can be made visible within a fraction of a second by secondary exposures.

The exposure which forms the image is a very intense radiation of wavelengths absorbed by the silver halide or it may be x-rays, gamma-rays or an electron beam, while the amplifying exposure is light-absorbed by the silver halide and is of moderate intensity. Good contrast between image and background and good stability of the background depend on the extreme reciprocity-law failure of these special emulsions, combined with their ability to be desensitized by low-intensity light. The contrast itself depends on the difference in light absorption between the silver of the image and nonimage areas. Properties of these direct-recording papers and mechanisms by which they function are discussed.

The need in modern engineering developments for materials to record data at very high speeds and the need to obtain access to such data in a minimum of time and with a minimum of chemical processing has led to the development of a new class of direct-writing recording papers. These new products have the unique ability of being processed entirely by radiant energy with no liquid or chemical steps, and, in the case of the Du Pont Lino-Writ 5 product, the developed image can be viewed within 1 sec of recording when the proper energy sequence is followed.

This product is used principally in the field of high-speed oscillograph recording of events which can occur in rapid sequence as during high-speed flight or missile operation. Writing speeds in excess of 40,000 in./sec can be obtained with direct-writing oscillographs having a high-intensity exposing light. This writing speed corresponds to an exposure of the order of 1 μsec.

These new papers present several distinct advantages over products previously described by Weyde[1] and Stabe[2] in increased sensitivity, more rapid access, higher image-to-background contrast and better image stability.

The image, present only in a latent or invisible form after the high-intensity exposure, can be amplified by the action of light to form a visible image. This apparent anomalous behavior—that is, both formation of the latent image and its development by light without complete loss through darkening of the background—is associated with the extreme low-intensity reciprocity-law failure of these emulsions. This effect can be best understood by an examination of the characteristics of this new type of emulsion.

It is known from the work of Lüppo-Cramer,[3] Debot,[4] and Berg[5] that, in general, intense exposure favors formation of latent images in the interior of the grains while low-intensity exposure forms surface latent images. The latter, or surface latent image, is the one normally developed by chemical development. In contrast, the internal image is not easily developed by such processing. The general effect of exposure time and intensity on the ratio between the internal and surface latent image in the direct-writing emulsion is shown schematically in Fig. 1.

The rapid writing speed of these new papers is obtained by enhancing the ability of the silver halide crystals to form internal latent images at high intensity in extremely short exposure times, for it is the internal latent image, rather than the surface latent image, that is intensified subsequently by absorbed radiant energy.

Proof that the latent image formed by the high-intensity exposure is internal was obtained using the techniques described by Dyba and Smith[6] and Stevens[7] (see Appendix I). The exposure used was a 10-μsec xenon flash through a step wedge and the speed was calculated as the reciprocal of the meter-candle-seconds necessary to form the first visible image. The highest speed was obtained when a

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1. Edith Weyde, *Z. wiss. Phot.*, **48**: 45 (1953).
2. H. Stabe, *ibid.*, p. 19.
3. H. Lüppo-Cramer, *Phot. Korr.*, **72**: 1 (1936).
4. R. Debot, *Mem. soc. roy. sci. Liège*, **6**: 91 (1942).
5. W. F. Berg, A. Marriage, and G. W. W. Stevens, *Phot. J.*, **86B**: 1052 (1946).
6. R. V. Dyba and T. D. Smith, *Phot. Eng.*, **7**: 98 (1956).
7. G. W. W. Stevens, *Phot. J.*, **82**: 42 (1942).

ferricyanide bleach was used to remove surface fog and the paper was developed in the presence of a silver halide solubilizing agent. In the absence of the solubilizing agent, the speed was low and only a weak image was formed, indicating that the latent image was largely internal. When both the ferricyanide bleach and solubilizing agent were omitted, a weak reversed image was formed, due to the high fog in the emulsion. Table I summarizes these results.

TABLE I. Latent Image Distribution and Effective Speeds

Internal development after bleach . .	25.*
Surface development after bleach . .	1.5
Surface development	1.5 (reversal)

* 1/mcs.

In the amplification or development of the latent image to a visible form, the energy used is the light absorbed by the silver halide in a second exposure rather than energy released by the reducing agents in normal chemical development. This light is ultraviolet and blue light, but must be of lower intensity than the exposing light. However, the energy absorbed—that is the intensity multiplied by the time—in this step is much greater than that used in forming the latent image. The intensity and time of exposure are in the region (Fig. 1) where little or no new internal latent image will be formed. This low-intensity amplification exposure, in addition, forms surface latent images on the nonimage grains, i.e., on those which did not receive the high-intensity initial exposure. These surface latent images apparently inhibit or prevent the formation of internal latent images. As a result the background is desensitized and is not easily darkened by further exposure to either high- or low-intensity radiation.

Although light not absorbed by the silver halide naturally does not affect the emulsion, the latent image, being silver, absorbs longer wavelengths of light. As shown in Fig. 2, there is some destruction of the latent image by exposure to yellow light before amplification.

To review the sequence of events that occur when this emulsion is used: first, the initial exposure is made with a high-intensity light source to form an internal latent image. Following this, the paper is given an exposure to light at a lower intensity for a longer period. During this second step, only the grains which were originally exposed become blackened while the remaining grains are desensitized by the low-intensity exposure.

Photographic Characteristics

This new type of photographic paper can be better understood by a more detailed study of its photographic characteristics, and some of these properties will now be briefly reviewed.

The light source commonly used in direct-recording oscillographs is an Osram high-pressure mercury arc HBO 107/1 with a flux of 2,000 lm. This light source is not easily usable when an H&D curve is desirable for analysis. For such a purpose, a xenon flashtube sensitometer was found more convenient. Models III and VI of the Edgerton, Germeshausen & Grier sensitometers provide flash exposure times of 10, 10^2, 10^3 and 10^4 μsec. Step wedges, intensity

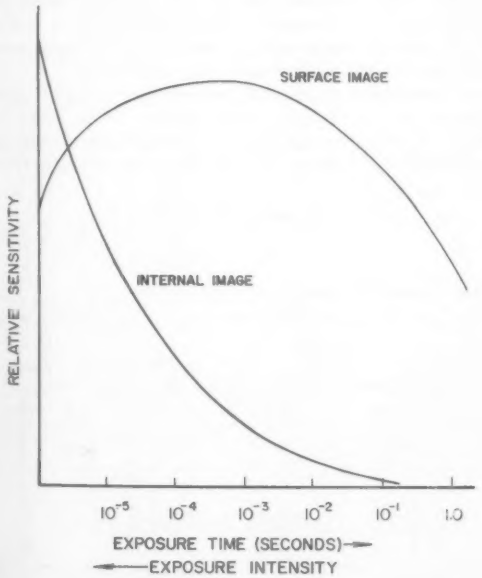

Fig. 1. Reciprocity effect on surface and internal sensitivity (equal energy exposures).

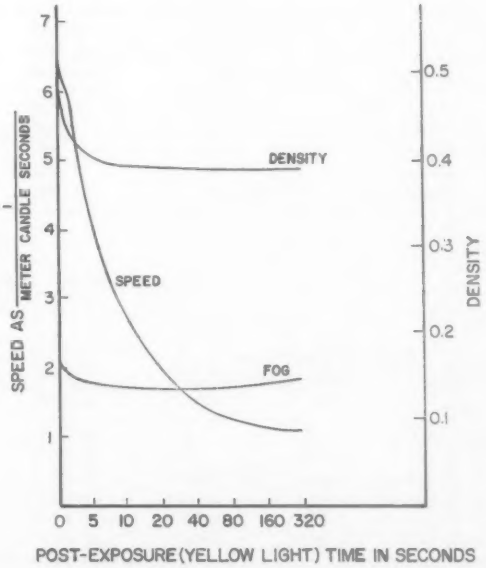

Fig. 2. Desensitization by post-exposure to yellow light. 40w white fluorescent lights (500 mcs) modulated by Wratten No. 8 Filter.

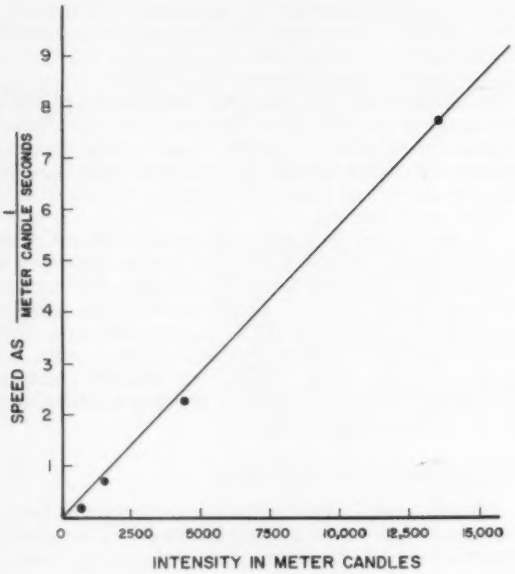

Fig. 3. Threshold speed as a function of exposure intensity.

compensating filters, and spectral filters can be used with these xenon flashtube sensitometers. Exposure values at the various exposure times available with such equipment are shown in Table II. Measurement of these exposures with a General Radio Type 1501A light meter confirmed the various values reported by Edgerton, Germeshausen & Grier in their operating instructions.

TABLE II. Edgerton, Germeshausen & Grier Sensitometers

Model	Exposure times, μsec	Meter-candle-seconds
Mark III	10	28
Mark III	1,000	2,800
Mark VI	100	130
Mark VI	1,000	7,000
Mark VI	10,000	1,300

Measurement of sensitivity at various exposure times was used to determine the reciprocity-law failure with decreasing intensity. Figure 3 shows the threshold exposure in terms of speed required to form a latent image. It can readily be seen from these data that the speed increases rapidly as the intensity is increased.

Amplification or formation of a visible image requires a lower intensity light exposure but more energy by a factor of 20,000 than is necessary to form the original latent image. A wide range of exposure sources for the amplification step can be used, from a 40-w fluorescent lamp at several feet distance to a photoflood lamp at close range. Table III lists the results in speed, fog, and image density when various amplification intensities are employed.

The highest amplification intensities resulted in fog nearly equal to the maximum image density, with a resultant low effective speed. Actually, in this latter case further exposure to room lights showed that additional density was developed in the background, presumably because the excessively high-intensity amplification exposure caused both internal latent image formation and image amplification. Table IV shows the results of amplification by means of a blue fluorescent desk lamp with and without various filters. When no filter was used, the radiation was too intense to result in good image speed. The filters reduced the amount of actinic light so that less fog and consequently more speed was observed.

Although the fog or background density can be kept low by using a very low-intensity amplification source, this increases the length of time before the image can be viewed. Some bleaching or fading of the latent image occurs during this longer period and the speed is, consequently, reduced.

A technique available to gain more rapid image access and maintain high speed is to heat the paper during amplification. This technique was also reported by Jacobs.[8] While the most effective speed

8. J. H. Jacobs, *Phot. Sci. & Eng.*, **5**: 1 (1961).

TABLE III. Reciprocity Effect in Amplification

Amplification[a,b] Intensity, m-c	Distance, in.	Time, sec	Reflection densities Image	Reflection densities Fog	Additional amplification[c] Image	Additional amplification[c] Fog	Effective threshold speed[d]	Image access time,[e] sec
2.9×10^6	3	4	0.47	0.45	0.57	0.54	0.07	4
7.2×10^5	6	16	0.49	0.46	0.56	0.45	0.2	4
1.8×10^5	12	64	0.48	0.35	0.49	0.37	0.9	4
4.5×10^5	24	256	0.50	0.30	0.50	0.28	2.3	8
1.1×10^4	48	1024	0.47	0.23	0.43	0.24	4.5	17
2.8×10^3	96	4096	0.47	0.18	0.44	0.19	9.0	36

a. Latent image exposure: 10-μsec xenon flash, Edgerton sensitometer.
b. Amplification exposure: Photoflood lamp No. 2 (17,000 lm, 3400°K) at room temperature.
c. Roomlight exposure after initial amplification (40-w white fluorescent lights at 6 ft).
d. 1/mcs.
e. Time for image appearance (not full amplification).

TABLE IV. Spectral Effects in Amplification

Two 15-w blue fluorescent tubes used at 6 in. for 64 sec

Filter	Cutoff, mμ	50% T, mμ	Image density	Fog density	Speed*
None	——	——	0.49	0.33	0.9
Wratten 2B	380	411	0.23	0.13	4.5
Wratten 2A	400	423	0.18	0.12	4.5
Wratten 3	420	464	0.04	0.04	——

* 1/mcs, 10-μsec flash, Mark III.

and contrast obtained at room temperature using white fluorescent lights is at intensities of about 500 m-c for 20 min, the amplification time with the Lino-Writ 5 paper can be reduced to 1 sec or less by amplification with a 10,000 ft-c photoflood lamp when the paper is heated to 120°C. Figure 4 shows the effect of temperature on speed at high amplification rates. This temperature effect is believed to operate through destruction of latent images or, more descriptively, of latent image fog centers formed by the more intense light used during the amplification. The result is that only internal latent images formed by the initial high-intensity exposure are capable of forming visible images, while the image centers formed during amplification never become stable enough to be amplified to a visible image.

Pre-exposure of the direct-writing emulsion to low-intensity actinic light desensitizes the emulsion strongly and causes a loss in writing speed and contrast after photodevelopment as shown in Fig. 5. With enough pre-exposure, sensitivity is lost entirely. This effect is, of course, the same action that occurs on the unexposed areas during image amplification.

Regression of the visible image or loss in contrast is an effect which occurs on prolonged absorption of light. The image, initially blue, reaches a maximum value, then slowly regresses and changes color. The image will last practically indefinitely if protected from prolonged exposure to strong light. However, if greater stability is desired, it can be obtained by a simple liquid preserving step.

Conclusions

The experimental results indicate that the effect of light on direct-writing emulsions is irreversible. An intense exposure forms many internal centers in a grain, each of which attracts products of subsequent photoreactions. These centers eventually grow into a size which absorbs considerable light falling on the grain and, because of their number, the optical density becomes great enough to be visible.

The background fog is lower than the image density when amplification exposure is of much lower intensity than the recording exposure. However, when a higher temperature is maintained during amplification, a higher light intensity can be used and the time required is decreased. These conditions apparently result in fewer centers which grow to a point at which they can effectively absorb light. The radiation tends to exhibit a sequential effect in that one center in the grain, or that part of a grain which forms a photoreactive unit, traps the effects of subsequent radiation.

Higher temperature during amplification aids the sequential effect by increasing the rate of formation of the active centers. Thus high-intensity light can furnish the products necessary to build up latent

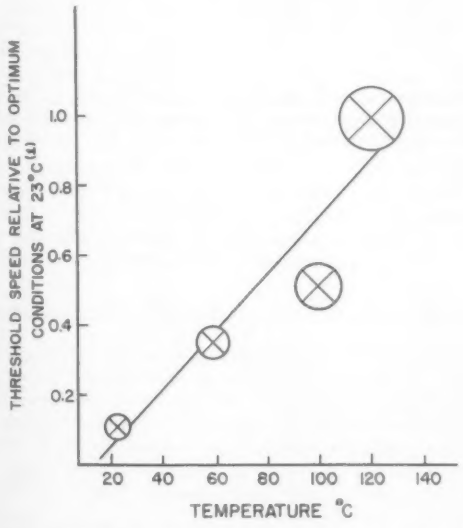

Fig. 4. Amplification at 110,000 m-c (access time < 1 sec). Note (1): 500 m-c white fluorescent lights for 25 sec.

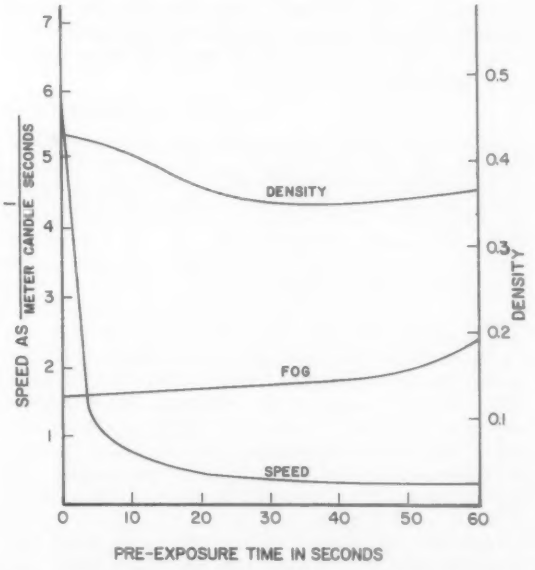

Fig. 5. Desensitization by pre-exposure to ultraviolet. 8-w G-E germicidal ultraviolet lamp at 10 in.

image centers already formed, but it does not allow as many new centers to form after the initial few in each grain are started.

As the centers grow and absorb light, a regression sets in—that is, the centers are transformed or broken up into a state which absorbs light less efficiently. This occurs in the fog areas as well as the image areas. Regression can also take place for the latent image before amplification; this is what is called the Herschel effect.

Table V summarizes in broad categories the major effects of light as a function of the order of exposure, intensity, and spectral composition.

TABLE V. Summary

	Blue and Ultraviolet	Yellow
Pre-exposure (low intensity)	Desensitizes	Inactive
Exposure (high intensity)	Latent image formation	Inactive
Post - Exposure (low intensity or high intensity at elevated paper temperature)	Amplifies latent images to visible images. Amplified images regress.	Herschel effect. Amplified images regress.

Direct-writing emulsions have been improved at a rapid pace of late and are in a position to replace developing-out emulsions for many applications. The impact of these materials on the field of oscillography has been dramatic, since they offer a convenient and reliable method to gain very rapid access to recorded information. It is felt that this is but the first of many uses, in some of which avoidance of wet processing and darkrooms may be more important than rapid image access.

Acknowledgment

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APPENDIX. Solutions and Procedure for Study of Latent Image Distribution

Solutions

A. Surface developer

Metol	2.5 grams
d-Isoascorbic acid	10.0 grams
Potassium bromide	1.0 gram
Sodium metaborate (Kodalk)	35.0 grams
Water to make	1 liter

B. Internal developer

Sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) added to above developer	3 grams

C. Bleach

Potassium ferricyanide	1.25 grams
Water to make	1 liter

Procedure

1. Surface development
   5 min at 20°C in Solution A
   5 min in acid hypo fix
   10 min wash
2. Surface development following bleach
   2 min in Solution C at 20°C
   20 min wash in running water
   5 min in Solution A at 20°C
   5 min in acid hypo fix
   10 min wash
3. Internal development following bleach
   2 min in Solution C at 20°C
   20 min wash in running water
   5 min in Solution B at 20°C
   5 min in acid hypo fix
   10 min wash

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The Interrupted Processing Method of Compensating for Exposure Errors in Aerial Photography

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A method of compensating for overexposure errors in aerial photography involves the use of "interrupted" processing in which the film is first developed to low photographic speed in a "primary" developer, inspected to determine the amount of image produced by this treatment, and then given supplementary "secondary" development to effect the requisite increase in speed up to that corresponding to full normal development. Procedures are described in which (1) the film is dried following primary development, permitting the use of conventional processing equipment, or (2) the film is examined or scanned continuously in the wet state after primary development, usually on a specially designed processor.

Exposure Considerations in Aerial Photography

Because of the uncertainty in advance estimation of correct exposure settings for high-altitude aerial photography, it is the usual practice to err on the side of overexposure to avoid total loss of shadow detail. Extensive surveys of military aerial negatives have shown that exposures are commonly so much in excess of an acceptable minimum that the concomitant increase in granularity and degradation of fine image structure cause a loss of important picture detail.

Although overexposure is often accidental, there appears to be a tendency to use exposure settings about 5 times, or 0.7 log, greater than the minimum for best quality with midday light conditions. If the lens aperture cannot be reset in the course of a mission, such an excess provides for the greater part of the profitable dawn and dusk periods, but it causes a loss in quality at higher sun angles. The practice of intentional overexposure may have resulted from the belief that a large exposure latitude exists.

Overexposure to this degree not only impairs image quality but results in excessively high density, especially with present-day high-contrast films. The printing of such dense negatives may be inconvenient and, with some printers, impossible.

Compensation in Processing for Exposure Errors

If overexposure of negatives could not be avoided entirely, it seemed that it might be possible to minimize the effects by modifying the processing to reduce the emulsion speed of the film. A study was made, therefore, of means for controllably reducing emulsion speed in development to lessen image-structure impairment and information loss. The use of reducing baths following regular processing did not produce acceptable results.

The practice of modifying the density characteristics of a negative by changing development conditions or the composition of the developer is nearly as old as photography itself. Previous to the widespread use of panchromatic materials, visual inspection during development was the usual practice.

With better estimation of exposure and the general use of time-temperature processing, development by inspection has practically disappeared. The difficulty of determining exposure requirements in aerial photography, however, appears to justify the adoption of some method of adjusting film speed on the basis of densitometric or visual observations in the course of development.

Maintenance of Contrast

Aerial photography at high altitudes usually suffers from the presence of atmospheric haze which degrades quality in the shadow region and may reduce the effective luminance scale to as little as 2:1, or 0.3 log E. In order to satisfy the most widely accepted requirements for negative contrast, films for this type of aerial photography are designed to give gammas of 2.0 or more.

It was thought to be desirable that a processing method designed to give reduced emulsion speed in aerial photography should be capable of maintaining practically full contrast. With older types of aerial negative films, when the time of development in the common developers, such as Kodak Developer D-19, was reduced sufficiently to yield only one-half of normal maximum speed, the contrast was reduced by 50%.

In 1954, experimental emulsion work resulted in the predecessor of the present Kodak Plus-X Aerecon Film and Kodak Plus-X Aerecon Film (Thin Base). The development characteristics of

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these films in D-19 are shown in Figs. 1 and 2. Reduction in time of development to yield one-half of normal maximum speed causes a lowering of gamma by only 25% for Plus-X Aerecon and 10% for Plus-X Aerecon (Thin Base).

It was pointed out by J. L. Tupper,* of these Laboratories, that it would be possible to take advantage of the constant contrast characteristics of these films to regulate the speed yield in processing and thereby compensate for overexposure while maintaining substantially full contrast. In order to determine the required speed yield, he proposed that the film be developed to considerably less than the maximum speed in D-19; treated in a stop bath; inspected visually by using an infrared source and an image-converter viewing device (Snooperscope); and then given supplementary development in D-19 if more image was required. With D-19 used in this way, when development was curtailed to effect a speed loss of 0.3 to 0.4, the contrast was still acceptable. However, if speed reduction to compensate for an overexposure as great as 0.7 log was required, the accompanying loss of contrast for most high-altitude negatives was excessive.

In 1955 the U.S. Air Force took advantage of the improved speed–gamma characteristic of one of these films to obtain selective reduction of speed for overexposed negatives.[1] The procedure involved inspection by an infrared technique following about one-third of usual development. By the use of a rather large and complex processing machine, the required supplementary processing was given, using a selectively programmed spray-application system. A stop bath was used to stay development during inspection.

Primary Developer

In more recent studies, it was found that hydroquinone-carbonate primary developers, with the addition of restraining agents, are capable of maintaining almost maximum gamma while reducing speed by as much as 1.5 log. The formula for Kodak Special Developer SD-42, designed to effect a 5-times or 0.7 log depression in speed, is given in Table I. For this degree of speed depression, the restraining action of bromide is sufficient, but organic restrainers are necessary if greater speed reduction is required.

Following primary development, the image can be inspected by infrared and secondary development given in D-19. The contrast is maintained while the speed is increased in any desired degree up to the attainable maximum.

Primary development, even in a heavily restrained hydroquinone developer such as SD-42, causes an increase in fog during secondary development in comparison with development to produce the same amount of image in D-19 without previous primary development. This increase in fog results in a $^1/_3$-stop loss in maximum attainable speed.

* Private communication.

1. "New Film Processor Developed for USAF," *Aviation Week*, p. 32, Nov. 26, 1956.

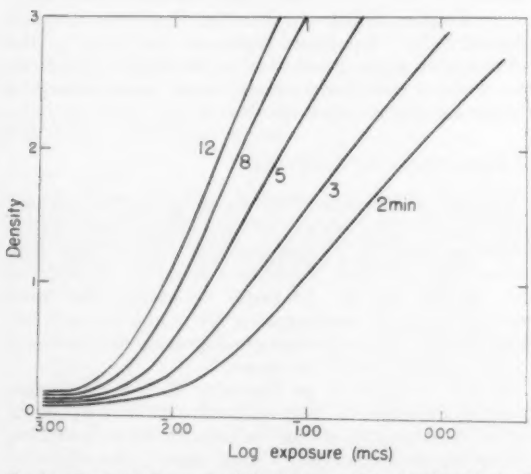

Fig. 1. Characteristic curves of Plus-X Aerecon Film, developed in D-19 at 68°F. Exposed to daylight.

Time of Development (min)	Gamma
2	1.18
3	1.35
5	1.80
8	2.28
12	2.48

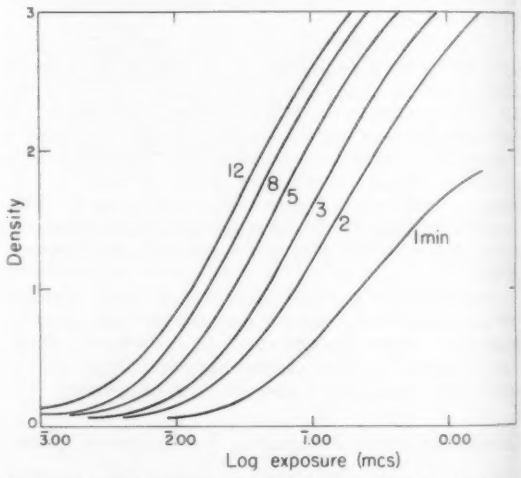

Fig. 2. Characteristic curves of Plus-X Aerecon Film (Thin Base), developed in D-19 at 68°F. Exposed to daylight.

Time of Development (min)	Gamma
1	1.12
2	1.62
3	1.74
5	1.82
8	1.84
12	1.86

Processing-Equipment Considerations

Three possible methods of using the processing procedure just outlined are:

(*1*). *Inspection on-the-run.* Visual inspection or densitometric scanning of the film follows primary development without further chemical treatment or drying before secondary development. It is assumed that the inspection can be performed quickly so that density does not grow significantly during the inspection.

(*2*). *Arrested primary development.* A stop-bath treatment follows primary development to provide more time for inspection.

(*3*). *Drying between primary and secondary processing.* Stopping, stabilizing, rinsing, and drying the film follow primary development to allow for more inspection time and facilitate the compensation of frame-to-frame exposure changes by cutting the film into lengths for various degrees of secondary development.

Choice of Method

Method (1) has the virtue of introducing the least complication chemically, the minimum increase in fog, and the least loss in maximum attainable sensitometric speed. The loss in maximum speed is somewhat less than that with Method (3), which involves drying following primary development. Method (1) is suitable in cases where exposure changes are not abrupt, since it is usually only possible to make changes in the degree of secondary development over a length of several feet.

Method (2) has the same advantages as Method (1), but allows more time for the inspection following primary development. Again, abrupt changes in secondary treatment are not usually possible.

Method (3), in which inspection is done in a separate operation, has the advantages over Methods (1) and (2) of permitting the use of processing machines without substantial alteration and allowing the maximum freedom in secondary development. Special equipment and considerable care are necessary in handling the incompletely processed film.

TABLE I. Formulas for Interrupted Processing[a]

Formula	Avoirdupois	Metric
KODAK SPECIAL DEVELOPER SD-42		
Water, about 125°F (50°C)	64 oz	500 cc
Hydroquinone	2 oz 290 grains	20 grams
Sodium sulfite, desiccated	6¾ oz	50 grams
Sodium carbonate, monohydrated	6¾ oz	50 grams
Potassium bromide	2 oz 290 grains	20 grams
Water to make	1 gal	1 liter
Dissolve chemicals in the order given.		
KODAK STOP BATH SB-5b		
Water	64 oz	500 cc
Acetic acid, glacial	4½ oz	35 cc
Sodium sulfate, desiccated[b]	6 oz	45 grams
Water to make	1 gal	1 liter
KODAK STABILIZER S-9		
Water, about 125°F (50°C)	64 oz	500 cc
Benzotriazole	1 oz 145 grains	10 grams
Potassium bromide (1% solution[c])	9 fluid drams	12 cc
Water to make	1 gal	1 liter

a. The chemicals used in these formulas should meet American Standard Specifications for Photographic Grade Chemicals.

b. If crystalline sodium sulfate is preferred to the desiccated form, use 2¼ times the quantities listed.

c. To prepare a 1% solution, dissolve 44 grains of potassium bromide in 10 fluid ounces of water at about 75°F (24°C) (1 gram in 100 cc of water).

Processing Recommendations

A detailed procedure is given in Table II. This procedure and the formulas given are applicable to both regular and thin-base types of Plus-X Aerecon. For use with Method (1), only the primary development, infrared inspection, secondary development, and all succeeding steps are used. For Method (2), the primary development, stop bath, rinse, infrared inspection, secondary development and succeeding steps are followed. For Method (3), the entire procedure as given in Table II is used. Kodak Stabilizer S-9 (see Table I) is used because the intermediate drying step tends to cause an increase in fog in secondary development. A short bath in a dilute solution of the wetting and antistatic agent Tamol-N† is used before the intermediate drying

† Rohm and Haas Co., Inc., Philadelphia, Pa.

TABLE II. Interrupted Process for Kodak Plus-X Aerecon Film and Kodak Plus-X Aerecon Film (Thin Base)

Treatment	Processing bath	Time (min) at 68°F (20°C)
Primary development	SD-42	7
Stop bath	SB-5b	1
Rinse	Water	1
Stabilize	S-9	2
Rinse	Water	1
Wetting agent and antistatic rinse	Tamol N[d] (15 grams/liter or 2 oz/gal)	1
Drying[e]		
Infrared inspection		
Secondary development	D-19	8
Stop bath	SB-5b	1
Fix	Kodak Fixing Bath F-5	3–5
Wash and dry	As required	

d. Rohm and Haas Co., Inc., Philadelphia, Pa.

e. Dry in rapidly moving dust-free air at a temperature not in excess of 100°F.

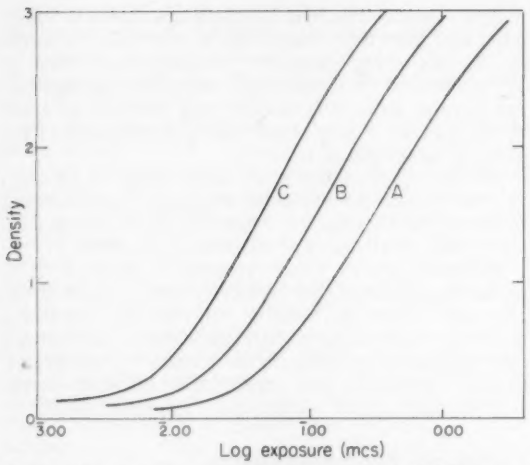

Fig. 3. Characteristic curves of Plus-X Aerecon Film (Thin Base), developed at 68°F. Exposed to daylight. Curve A—developed for 7 min in SD-42; Curve B—developed for 7 min in SD-42 followed by 1 min in D-19; Cu ve C—developed for 7 min in SD-42 followed by 8 min in D-19.

to help retard a tendency to static electrical marking. Figure 3 shows the curves obtained for Plus-X Aerecon Film (Thin Base), using Method (3). Curve A is for primary development only. Curves B and C represent the effect of primary development followed by 2 degrees of secondary development.

Control of Image Density

If this system is adopted for aerial photography, it is necessary to choose a formula and degree of development for the primary development which depresses the speed to a degree which will compensate for the maximum degree of overexposure prevailing in normal operation. For the typical case of 0.7 log compensation, the desired speed depression is obtained with 7-min primary development in SD-42. Density in the shadow region for a 5-times overexposure will be at a level of about 0.3 above fog where gradient is sufficient for acceptable tonal separation and image-structure loss will be minimized. At the same time, the maximum highlight density for the prevailing type of subject and haze condition will not usually be excessive. All lesser exposures yield shadows ranging from this point down to fog level.

If the only consideration in deciding the need for supplementary development was the avoidance of excessive highlight density, the assignment of secondary development would not be very difficult. However, because the luminance scale may vary considerably, the need for increased speed must be based on shadow densities where the gradient is low so that relatively large speed changes correspond to small density differences.

The amount by which speed can be increased with confidence in one secondary development stage is, therefore, determined by the accuracy with which the shadow density of the partially developed negative can be determined, the contrast of the film, and the permissible upper limit of highlight density in the finished negative. An error of 0.05 in reading the minimum density of an underexposed negative which has received primary development to product the characteristics shown by Curve A of Fig. 3 might correspond to as much as 0.5 uncertainty in shadow density when the 8-min secondary development is used. Even greater uncertainty in highlight densities wholly on the straight-line portion of the sensitometric curve is involved. Determination of density within 0.05 in the inspection step is difficult.

By interposing a second inspection after an intermediate degree of development corresponding to Curve B of Fig. 3, the uncertainty in final density is reduced to about 0.15. Therefore, depending on the precision with which negative density must be controlled, cases may arise where it is necessary to repeat the inspection following partial secondary development. However, drying the incompletely processed film a second time with a consequent increase in fog and handling complexity would seldom be justified.

Effect on Image Structure

Image-structure studies on overexposed films that have been processed using these methods of obtaining reduced emulsion speed have shown a worthwhile degree of improvement over those given full, normal development with consequent excessive density. Granularity was reduced by about 40%, and resolving power and image sharpness were significantly increased. In fact, the latter two were slightly higher in a negative which received only primary development than in a properly exposed negative given normal D-19 development.

For cases in which the available exposure is predictably 5 times greater than required with Plus-X Aerecon Film, it would be reasonable to expect that better image structure could be obtained with slower films of inherently finer grain. This assumes, of course, that the film characteristics are the limiting factor in the photographic system.

Discussion

The interrupted process offers some advantage as a salvage technique if overexposures of known magnitude occur at unpredictable intervals, but imposes onerous requirements for equipment and skill of personnel. Therefore, the methods and techniques described are not recommended except when unavoidable overexposures must be compensated for. Further effort might well be devoted to improvement of automatic exposure-control methods to minimize the occurrence of overexposure in aerial photography.

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• Short Communications

Rapid Dry Development of a Silver-Sensitized Recording Paper

P. H. STEWART, W. BORNEMANN, AND W. B. KENDALL, *Research Laboratories, Eastman Kodak Company, Rochester, N.Y.*

Rapid dry development of oscillograph traces in a new silver-sensitized recording paper has been achieved using a processor of simple design. The new paper contains all the necessary developer chemicals incorporated in the emulsion. The processor is a heating chamber entirely enclosed, except for slits at the front and back for exposed material to enter and leave. Processing is initiated by moisture driven from the emulsion and base which condenses on the cool surface of the entering emulsion. The combination of increased moisture and rapid application of heat causes development to occur within a few seconds.

The new paper, now labeled "Kind 1549," shows a high degree of low-intensity reciprocity failure, as illustrated by the curves in Fig. 1. This reciprocity failure

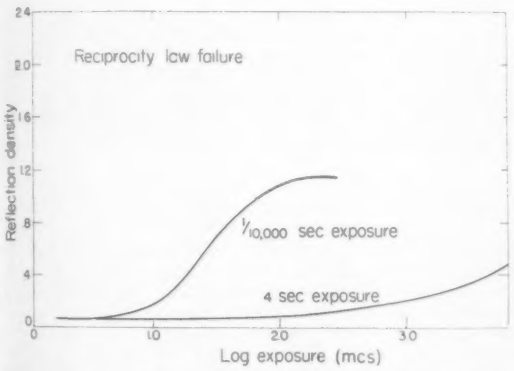

Fig. 1. Sensitometric characteristics of Kind 1549 paper under two different exposure conditions.

is an important feature of the paper, since it provides relatively high speed and contrast in an oscillograph where high spot velocities result in short exposure times, but it tends to suppress fogging by flare light inside the instrument and by accidental exposure outside. The paper has adequate speed to record at writing speeds up to 10,000 in./sec when used in a Honeywell 906 Visicorder,* which is equipped with a high-pressure mercury-vapor lamp (Osram HB 107) and quartz optical parts.

Communication No. 2126 from the Kodak Research Laboratories, presented at the Rapid Processing Symposium, Washington, D.C., 14 October 1960. Received 15 November 1960.

* Manufactured by the Minneapolis Honeywell Regulator Co., Heiland Div., Denver 22, Colo.

In a Midwestern D/R Recorder,† which has the same lamp but glass optical parts, the maximum writing speed is about 5000 in./sec. The paper has only about $^1/_{100}$th the speed of Kodak Linagraph 480 Paper, however, and is too slow for use in recorders equipped with low-voltage tungsten lamps.

Development of Kind 1549 is accomplished by the same mechanism that operates in ordinary photographic development of silver halide materials, and a limited amount of water is all that is needed. The water could, of course, be supplied by "immersion" in air saturated with moisture, by exposure to a jet of steam, or by immersion in hot water. The paper, however, contains all the water that is needed if it is used efficiently, and this is accomplished by the help of suitable mechanical equipment.

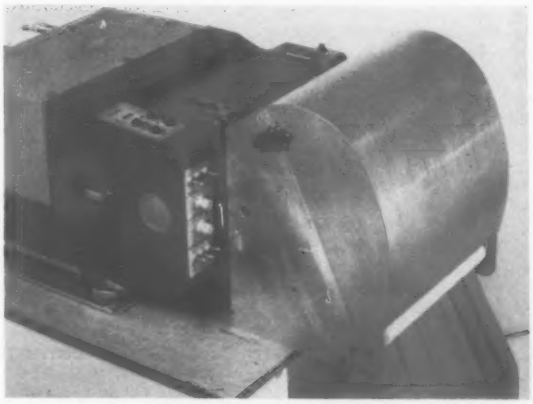

Fig. 2. Laboratory model of Kind 1549 paper processor attached to Midwestern D/R Recorder.

A laboratory model of a machine built to develop 12-in.-wide rolls of Kind 1549 paper is pictured in Fig. 2 and shown diagrammatically in Fig. 3. Essentially, it is a chamber completely enclosed, except for provision for the paper to enter and leave. The curved bottom plate is of smooth metal and is equipped with four 350-w heaters along its 21-in. length. The roof is another metal sheet, spaced just 0.5 in. above the bottom plate, and is equipped with four 160-w heaters. The roof is hinged at its lower end to provide access to the inside

† Manufactured by Midwestern Instruments, Tulsa, Okla.

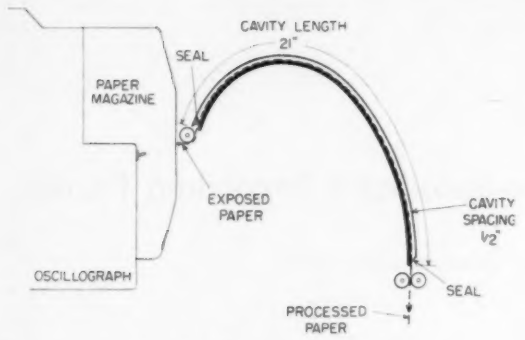

Fig. 3. Schematic diagram of laboratory model processor.

of the machine and to facilitate threading the paper. When closed, it presses against vapor-tight rubber gaskets on either side of the bottom plate. At the entrance and exit to the cavity formed when the roof is closed are flexible rubber seals which, though not stiff enough to damage the emulsion, are tight enough that a small vapor pressure (approximately 0.006 lb/sq in.) may be built up inside the chamber. A pair of drive rolls is located just below the exit to pull the paper through the processor. When the machine is operating at the rate of 25 ft/min or less, the temperature of the bottom plate is usually adjusted to about 240°F. At higher speeds, however, bottom plate temperatures as high as 300°F may be required to ensure sufficiently rapid transfer of heat from the plate to the emulsion layer through the paper base. Heat from the roof does not contribute to the development process. The roof is maintained just above 212°F solely to prevent condensation and consequent loss of moisture from the chamber.

As an exposed web of paper passes through the machine, the emulsion first gains moisture and then is developed and dried. Drying stops development. The moisture gain results from condensation, on the surface of the relatively cold entering paper, of water which has been evaporated from paper that previously passed through the processor. Thus, if the processor is running continuously, an external source of water is not needed to increase the moisture content to that required for development. On start-ups, about 5 ft of paper must be run before good development is achieved; alternatively, the chamber may be precharged with a few drops of water, in which case development is obtained immediately. Image development is quite complete at operating speeds up to 35 ft/min (equivalent to 3 sec or more in the chamber). Development is less complete at higher speeds but might be considered adequate for some uses.

Prints prepared according to the methods outlined are, of course, unfixed. Furthermore, the developer remaining in the background areas is still essentially as active as it was before the paper was processed. Consequently, if the prints are fogged by exposure to ambient light, the background tends to darken because of developing and printing-out. Nevertheless, these unfixed prints may have considerable utility. Oscillographic traces, fastened to a wall in a laboratory where relative humidity is maintained at approximately 50%, print out to a low-density brownish background within a few hours after they have been exposed to light; but, in ensuing periods of several months, further changes in the appearance of the prints are small. The brown background does not seriously impair legibility. As atmospheric conditions become more humid, fogged areas of prints darken faster to a more neutral color as the result of the formation of increasing amounts of developed silver, along with print-out silver. Owing to the reciprocity-law failure characteristic of the emulsion, however, oscillograph tracings remain legible at the extreme condition of 100% RH for about 30 min in bright room lights. Image degradation may be halted at any time by fixing or stabilizing the emulsion by ordinary wet procedures.

Coming Technical and Scientific Meetings

(*Continued from page 97*)

Institute of Radio Engineers, PGIT, International Symposium on Transmission and Processing of Information, September 6–8, Massachusetts Institute of Technology, Cambridge, Mass.

International Congress for Scientific Photography, September 11–17, Zurich, Switzerland

American Roentgen Ray Society, September 26–29, Deauville Hotel, Miami Beach, Fla.

90th Semiannual Convention, Society of Motion Picture and Television Engineers, October 2–6, Lake Placid, N.Y. Papers Chairman, C. Loren Graham, Kodak Park, Bldg. 65, Eastman Kodak Co., Rochester 4, N.Y.

American Photoengravers Association, October 8–10, Penn-Sheraton, Pittsburgh, Pa.

Optical Society of America, October 18–20, Biltmore Hotel, Los Angeles, Calif.

International Symposium on Photoelasticity, October 29–31, Chicago, Ill.

Society of Reproduction Engineers, Visual Communications Congress, December 1–4, Hotel Biltmore, Los Angeles, Calif.

91st Semiannual Convention, SMPTE, April 30–May 4, 1962, Ambassador Hotel, Los Angeles, Calif.

1962 Annual Conference, SPSE, May 7–11, Somerset Hotel, Boston, Mass.

92nd Semiannual Convention, SMPTE, October 22–26, 1962, Drake Hotel, Chicago, Ill.

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•Discussion and Evaluation

Future Military and Commercial Applications of Rapid Access Photography

EDWARD K. KAPRELIAN, *U.S. Army Signal Research and Development Laboratory, Fort Monmouth, N.J.*

It is probable that we will soon achieve substantially instantaneous photography, i.e., rapid access photography, producing a negative or a print or a transparency having photographic characteristics indistinguishable from the normally processed item, and available in a fraction of a second.

Assuming that this accomplishment will be realized within the next five or ten years—and it must be if photography is to hold its lead over and indeed to survive electronic competition in the rapid access field—a number of new applications and many extensions of old applications, both military and commercial, will evolve.

First, because of the many image-forming processes which exist, it is desirable at this point to distinguish photography from the quasi-photographic technique. For the purposes of this presentation a photographic process, or more appropriately, a photooptical process, is one in which a radiant energy image from an object is recorded in more or less permanent form in the simultaneous mode on a surface possessing responsiveness to the energy.

This definition includes silver halide photography, electrophotography, Kalfax, and all the usual forms of photography. Thermoplastic recording, normally excluded from the definition in that it operates in the sequential mode and does not employ radiant energy from the object, might qualify in the exceptional case of direct recording in an electron microscope. Magnetic recording, also normally excluded for the same reason, might qualify in one known system where a heat image drives portions of a premagnetized recording surface past the curie point to yield a latent image of varying magnetic fields. Depending upon the manner in which they are employed, the use of a layer of NCR microcapsules might or might not qualify as a photographic process.

After we have determined what can be done with very rapid access, or immediate access, photography, when available, and decided whether it is worth going to the trouble, we will re-examine the various processes to learn how close the present state of the art has brought us to the goal.

Military and Management Applications

Rapid effective decision-making for both military and management operations becomes increasingly more critical as the reaction time available to the military commander or to the industrial operations manager is reduced, as the mass of necessary input information or data expands, or when the sources of information and the operation center are geographically separated. In an effective decision-making system comprising men, machines, and methods, the men can organize, control, and use the system, provided the machines can process, store, and present information quickly and in adequate detail, and provided further that the methods can correctly link the men and the machines. Five essential steps are involved: *collection* (obtaining photographs, maps, printed pages); *reduction* (conversion of selected information into a specific, utilizable form); *manipulation* (comparison, evaluation and/or combination of reduced or converted information); *storage and retrieval* (retaining for future use and making available as needed); and *presentation* (display of charts, photos, reports, etc., dynamically or statically).

In each of these steps, rapid access photography can play a dominant role. In the collection step, pictorial recording is competitive with other methods, such as magnetic tape and punched cards. In reduction, photography could well be the best procedure, depending upon system requirements and characteristics. For the storage step, the photographic method has the advantages of permanence and high information density. In retrieval, the print-out of information from storage onto photographic materials is efficient and clearly competitive to other methods. In presentation, projection from a photographic image is attractive and efficient, especially if large displays are required.

In some way, each application, whether military, commercial, or miscellaneous in character, partakes of one or more of these steps.

Rapid access photographic surveillance from an airborne vehicle is a logical application to the collection step; it permits real-time operation in surveillance from drones or manned aircraft.

In the instantaneous photo display system, the image on a PPI scope is recorded on film and immediately projected; this obviously employs the collection step and the display step, without reduction and manipulation.

In side-looking radar, immediate access to the photographic image will not only increase the value of both telemetered and visually employed data, but conceivably may permit use of image data as a navigational aid under some circumstances.

In optical correlation radar, successive radar returns, each including target information plus noise or clutter,

Presented at the Rapid Processing Symposium, Washington, D.C., 15 October 1960. Received 26 October 1960.

are stored and correlated. Substantially immediate access to the photographic image would permit the low-velocity sensitivity of high-resolution radar to be maintained while yielding an almost real-time output to be data-linked to the ground.

Manned or unmanned airborne or space vehicles including unmanned drones and unmanned reconnaissance satellites could telemeter real-time meteorological data, permitting the correlation of their several simultaneous outputs. Terrestrial and lunar observation should be equally possible.

Manned bombers would be capable of providing ground stations with bomb damage information in real time (even over appreciable distances, with the use of one or more relay links) for immediate evaluation. Supplemental tactical action could be taken while the original mission was still on its return flight.

In missile test-data acquisition, the highly accurate instrumentation recordings will become even more valuable than at present, if rapid access without loss of accuracy is achieved. Immediate readout of data followed by high-speed computer techniques will allow prompt application of data, possibly even as feedback to the same missile.

The applications to battlefield surveillance, employing photographic cameras or infrared sensors, are obvious. Immediate telemetering of only the militarily significant portion of the image would require reduced bandwidth and/or reduce the time for transmission of the needed information. Note that in all telemetering systems, the rapid access characteristic is as essential to the ground or home installation as it is to the original photographic recorder, if approximate real time is to be achieved. Other military applications include: high information density displays of a composite type which combine various kinds of graphic information from different sources (multiple-channel type) for simultaneous presentation; display systems for the superimposition of, for example, radar data and character data, without external memory or time sharing.

There are a large variety of applications which are of both military and commercial interest. Facsimile is one of the techniques, the value of which is enhanced with the possibility of immediate availability of the received information. The superior sensitivity and informational capacity of most photographic materials far exceeds that of electrosensitive papers, permitting simpler, lower power recorders, and smaller image size for the same informational content.

Medical and Legal Applications

In photographic dosimetry, in endoscopic and ophthalmoscopic photography, in medical and dental radiography, in color-translating microscope techniques, and in other applications relating to medicine, immediate access may permit long distance diagnosis and rapid action, resulting in reduction of human suffering and loss of life. Thus, small or isolated hospitals or dispensaries can receive x-ray film interpretation and other diagnostic help from larger and better staffed hospitals and clinics. The use of facsimile techniques is sufficiently error-free to make this approach feasible.

In law enforcement and in the provision of security information, rapid access would permit new and more effective techniques to be employed in the identification of personnel, handwriting, fingerprints, etc.

Some General Applications

What was stated in regard to missile data applies equally well to the immediate availability of data in high-speed motion pictures, to motion-picture data records generally, and to photoinstrumentation records where it may be possible to read out an immediately accessible photographic record, apply a change or correction based upon the latter, and continue to record the same action without interruption.

Immediate access to the data on a spectroscopic film likewise permits one to think in terms of entirely new techniques in analysis and control of chemical and metallurgical processes.

As computers evolve they will increase in speed, in memory capacity, and in volume of input and output, while at the same time becoming smaller in size. The recording of computer output will become more difficult in the face of the need to satisfy mutually exclusive requirements: immediate availability of output, high informational volume, and small size of output recorder. Rapid access photography on high-resolution film and substantially simultaneous projection following recording would satisfy these requirements. Rapid access photography could also become the most versatile and practical method of providing whole new memories for some electronic computers. Potentially, it is as rapid a technique as any in existence and superior to most others because of its high information density and unusual permanence.

Rapid access photography should also eventually prove a value in adaptive control, wherein an organism alters itself to fit changing external conditions. As the inputs to an adaptive control system become highly complex and extremely voluminous, rapid access photography may well be the desirable way to operate a "learning model."

Other possible applications of a more general nature include interstate business transaction transmission, as in stock exchange trading situations; large theatre television with real-time projection from a film intermediate; and automatic photographic exposure control. There is also the burgeoning field of duplicating and copying. The present intense need for copies in office work will continue to increase in coming years because of the unavoidable demand for complete and detailed paper work in the government, in the military, in records, reference, and correspondence in social benefits administration, and in revenue administration. Because the duplicating and copying rate per machine or office worker must improve, the time needed per copy must be reduced. At present, the transfer processes and xerography must take second place in both speed and convenience to the desk-top thermographic copier for many routine uses.

Surveillance cameras installed in banks and elsewhere would be of greater value if immediate access to the photograph could be had. The chances for immediate apprehension of the suspect would be enhanced, an idea not especially encouraging to a would-be law breaker. Horse racing has long enjoyed the impartial judgment of photographic installations at the racetrack. Another sport which might benefit by an extension of this idea is baseball. Motion-picture cameras (high speed if required) covering home base and each plate would become actuated, either automatically or manually, when the ball entered the field of view, and the objective results of the particular play could be announced immediately without reliance on human judgment.

The Direction of Future Developments

Obviously, both the known and the potential applications are numerous and challenging; these alone are powerful incentives to achieve immediate access photography. There is another and probably equally powerful incentive, however, to a large number of photographic scientists and engineers: the fear of obsolescence of conventional photography for rapid access use. The true photographic or photooptical processes such as silver halide photography possess many advantages over other methods: high sensitivity, panchromaticity, high information recording density, permanence, low cost of duplication, moderate cost, good shelf life, convenience of processing, and convenience of readout. Yet, because of the single outstanding disadvantage of the silver halide system—the lack of immediate availability of the developed image—electronic or quasi-photographic methods may prevail. Once such other methods become largely accepted,—as, for example, might well occur in the employment of electronic recording inputs in computing systems where heretofore photooptical inputs have been standard—techniques will evolve permanently in the direction of electronic input.

Evaluation of Present Processes

Just how closely rapid access silver halide photography has approached the immediate access goal is difficult to establish because it is not possible to compare and evaluate the different systems; each is almost unique. The different systems employ different films, produce different maximum densities and gammas, and alter the "normal" film characteristics differently. Thus one high-temperature system capable of producing an image on 35mm film which is accessible in less than 0.5 sec is neither superior nor inferior to another which makes available the developed information on 5-in. or 9-in.-wide serial film in 8 or 10 sec; the image characteristics are simply not comparable. Notwithstanding this, the usual silver halide materials continue to offer the promise of much shorter access times.

The diffusion transfer process may provide its own solution to the problem of rapid access. The recent reduction of processing time in the Polaroid-Land process from 1 min to 10 sec is probably not nearly the limit of rapid availability of the image.

Attempts have been made to accelerate the processing of color film to the point of producing rapid access color photography. There appears to be some promise for two-color emulsions and the present goal is 5- to 10-sec access.

The electrophotographic process is inherently well suited for rapid access, and arrangements employing powder cloud development and aerosol sprays have been employed with rather brief access times. Described in the patent art are still other electrophotographic techniques which, with further development, appear to offer the possibility of achieving processing times of considerably less than 1 sec.

Photooptical systems other than the silver halides and electrophotography hold ultrarapid access potential for the future, with or without inherent limitations; Kalfax and the NCR microcapsules are good examples. Still other photooptical systems have long existed which, with the availability of today's techniques and materials, offer possibilities for rapid access in special applications.

The nonphotographic or quasi-photographic systems, although lacking the advantage of simplicity possessed by the photooptical methods, include developments which promise very rapid access to recorded information. The General Electric Company's thermoplastic recording, as a recent example, depends upon a modulated flow of electrons, and records in the sequential mode, in contrast with the simultaneous mode of conventional photooptical systems. Its information density of 40 million bits/sq in. compares with the best photographic practice and exceeds by two orders of magnitude the capability of present magnetic recording. The recording time is less than 0.01 sec, and the readout may be optical or electrical. The thermoplastic surface on which the electrostatic charge pattern is written by the electron gun is developed by heating to produce deformations, and then cooled to retain the ripples which constitute the recording. The thermoplastic surface is erasable and reusable, by reheating to a temperature higher than that used for recording. The recording can be in the form of an image which can be projected through use of an optical system provided with occluding bars similar to that in the Eidophor television projection system. It is usable for color recording and reproduction. The General Electric Company claims that at present large screen display of radar signals can be recorded and projected in less than 1 sec.

There is no doubt that this technique can be speeded to reduce access time to a small fraction of a second. Also, other sequential-mode recording systems of a nonphotographic nature, such as magnetic tape recording, can be combined with known presentation techniques to yield access time of less than 1 sec.

These are some of the systems with which photooptical methods must compete successfully in the future, on the basis of short access time. They represent the challenge which the photographic scientists and engineers must meet.

• Book and Journal Reviews

Memoirs of a Photochemist

FRITZ WENTZEL, edited by Louis Walton Sipley, American Museum of Photography, Philadelphia, Pa., 1960, xii + 146 pp., $10.00.

Memoirs of a Photochemist is more than just autobiography. The author's account of his life, which covers his early years as a student and his subsequent professional connections with several manufacturers of photographic materials in Germany, Belgium, Czechoslovakia, Spain, and the United States, is used as a framework for a series of technical, historical, and biographical briefs on photographic technology and some of its outstanding scientific personalities. The account ends with Dr. Wentzel's retirement, in 1946, from his position as head of the Ansco Paper plant.

The book is published as a feature of the 20th Anniversary of the American Museum of Photography. The editor states that he has endeavored to preserve the charm and simplicity of expression which characterizes Dr. Wentzel's writing, while at the same time making minor rephrasing to remove evidences of German grammatical structure. In this, the editor has succeeded for the most part, although he has only partially eliminated the German form of certain technical names. Thus, we find in places, but not consistently, the chemical names of salts appearing as one word (e.g., silvernitrate, bariumchloride); acetone spelled without the terminal "e," and micro photograph used where photomicrograph is intended. A few minor errors were noted, e.g., the numerical values given on page 16 should be labeled millimicrons, not angstroms; on page 54, "hydrogen sulfite" should be hydrogen sulfide; Momme Andresen was born in 1857, not 1847 as given on page 125.

Memoirs of a Photochemist is well worth reading for its biographical, historical, and technical content. It is illustrated with photographs of many of the men whose contributions to photographic science and technology are touched upon in its pages (e.g., Vogel, Traube, Miethe, Goodwin, Eder, Fischer, Lüppo-Cramer, and Luther) and with photographs of manufacturing equipment and laboratories. Sixteen pages of references and notes, together with an extensive index, add to the value of the book.—*T. H. James*

Instrumentation and High-Speed Photography

Volume 1, Series II, Society of Motion Picture and Television Engineers, New York, N.Y., paper bound, 187 pp., 8 by 11 in., $4.00.

The publication of this compilation of papers from the *Journal of the SMPTE* (1955–1960) adds to the more than one thousand pages devoted to this field of photographic technology in the six volumes of the First Series. The book contains 43 papers on light sources, optics and visibility studies, cameras and accessories, the properties and uses of cathode-ray tubes, television systems in instrumentation, very high-speed systems, processing and processing machines, and applications in military and industrial test programs. Extracts from SMPTE Progress Reports for the years 1956–1959 are included, together with abstracts in French and German of all of the reprinted papers.

Zhurnal Nauchnoĭ i Prikladnoĭ Fotografii i Kinematografii

Vol. 5, No. 4, July–August 1960 (in Russian)

Résumés by S. C. Goddard

The Influence of the Concentration of Developing Agents on Rapid Development: II—A Study of the Hydroquinone Developer

V. A. VEĬDENBAKH AND P. I. LEVINA, pp. 241–46

In Part I (*Zhur. Nauch. i Priklad. Fotografii i Kinematografii*, **5**: 20, (1960)), the action of Metol was found to be not completely explicable by the electrochemical theory of development. It seemed possible that this was because the uncharged amino groups were capable of penetrating the charge barrier and adsorbing on to the silver halide surface. Experiments have now been carried out with hydroquinone which possesses two negatively charged groups in the para positions. The results obtained differ significantly from those with Metol. The differences are shown in the form of the density against log concentration curves for the developing agents and by the restraining action of potassium bromide on the hydroquinone. There was no difference in the mechanism of fog formation with the two developers.

The Influence of Some Factors on the Tendency to Halation and Resolving Power of Photographic Materials

I. A. NOVIKOV, pp. 247–54

Methods have been worked out for the quantitative evaluation of halation arising in graphic arts materials as a result of scattering and reflection. The following points have been made by the use of these methods:

(1) Diffusion halation spreads wider with short times of development, agitation of the developer, increase in the concentration of gelatin in the emulsion layer and decrease in the thickness of the layer, the gelatin/silver ratio remaining constant.

(2) The intensity of halation by reflection decreases with increase in the coloration of the antihalation layer and with the thickness of the emulsion layer, while keeping constant the difference between the indices of refraction of the base and antihalation layer, and also with decrease in the length of exposure.

(3) Halation due to diffusion and resolving power does not change uniformly under the action of a number of factors. Apparently the different modes in which the above characteristics change are caused by factors having an influence on the distribution of the image silver in the thickness of the photographic material. (*Translation of author's abstract*)

A Recording Densitometer for RDTsB-1 Color and Black-and-White Photographic Papers

A. N. USPENSKII, pp. 255–61

The apparatus described is a semi-automatic recording reflection densitometer. Constructional details are given

and the method of calibrating the apparatus is described. The accuracy of the instrument is discussed.

The Principles of Preparation and Properties of Ultra-Fine-Grain Emulsions for Nuclear Research

N. A. PERFILOV, E. I. PROKOF'EVA, N. R. NOVIKOVA, O. V. LOZHKIN, V. F. DAROVSKIKH, AND G. F. DENISENKO, pp. 262–73

A summary is given of work on the preparation of ultra-fine-grain nuclear emulsions, some of which has already been reported in more detail. Formulae and method of making the emulsions are briefly set out. The potentiometric control of pAg and pH is described. The properties of the emulsions prepared by the authors are discussed, including keeping qualities, response to treatment with triethanolamine, retarding effect on charged particles, sensitivity to light, and track-recording properties. A standard blank form is proposed for recording the sensitometric properties of the emulsions and determining the track density. Finally, a mathematical expression is derived for the relation between the grain density and the specific energy loss.

The Luminescence Photography of Documents

N. M. ZYUSKIN, pp. 274–79

The photographic aspects of the examination of documents by fluorescence are discussed, including the choice of light sources, filters, and photographic materials. Visible luminescence produced by ultraviolet radiation and infrared luminescence produced by visible radiation are both dealt with.

Exposure Time in High-Speed Cameras with Compensating Prisms

E. A. TARANTOV AND YU. A. TSVETAEV, pp. 280–88

A mathematical analysis is made of the exposure of film in a high-speed camera using optical compensation by means of a rotating prism. The Soviet SKS-1 high-speed camera can easily be altered so that the partial exposure time (i.e., the exposure time for any individual part of the frame) can be varied without affecting the frame frequency or the total exposure time for the frame as a whole.

The Stereophotography of Flow Lines from a Flat-Keeled Plate Gliding on a Free Water Surface

A. G. NIKOLAENKO AND V. I. RYBAKOV, pp. 289–92, 2 pl.

Reciprocity of Time and Intensity of an Electron Beam in the Irradiation of Type MK and MR Photographic Plates

I. A. FOMINA AND K. S. BOGOMOLOV (Letter to the Editors), pp. 293–94

Recently MK and MR plates prepared by NIKFI have been used for electron microscopy. They have a high resolving power because of their fine grain and very small intergranular distance, but their sensitivity is not inferior to those normally used in electron micrography. Reciprocity failure in photographic materials used for electron micrography is thought to be due to the excitation of grains by more than one electron. Calculations show that for the new plates the ratio of grains excited by more than one electron to grains excited by only one electron is very small. Experimental confirmation shows that in fact both plates have no detectable reciprocity failure for long exposures.

The Stabilizing Action of Thiazolotetrazoles and Benzothiazolotetrazoles on Silver Chloride Emulsions

L. F. AVRAMENKO, YU. B. VILENSKII, L. K. GUSEVA, B. M. IVANOV, V. YA. POCHINOK, Z. I. STEKLYANNIKOVA, AND G. P. FAERMAN (Letter to the Editors), pp. 294–95

Substances used as stabilizers in silver chloride emulsions show a pronounced desensitizing action. They may also decrease the effect of optical sensitizers. It was thought that this effect was due to the acid dissociation of the molecules and therefore an attempt was made to find stabilizers among compounds without an acidic hydrogen atom. Thiazolotetrazole and its derivatives did not stabilize silver chloride emulsions and did increase fog. Only 4-phenylthiazolotetrazole showed a slight stabilizing action. Benzothiazolotetrazole and its fluoro, chloro, bromo, phenyl, methyl, *tert*-butyl, and acetimido derivatives in the 6-position, and also the 6,7-phenylene derivative strongly stabilize silver chloride emulsions and lower fog. They desensitize to different degrees. 6-methoxybenzothiazolotetrazole in its optimum concentration shows practically no desensitizing action. The substances studied give a weak desensitization in silver bromide emulsions, on which they have no stabilizing action. The mechanism of the interaction between benzothiazolotetrazoles and silver halides has been studied.

The Problem of the Reversibility of the Desensitizing Action of Moisture on Photographic Materials

K. V. VENDROVSKII AND V. I. SHEBERSTOV (Letter to the Editors), pp. 295–96

Under the action of water vapor the sensitivity of a photographic material falls, but, on drying, the original sensitivity is regained. Experiments on a high-speed ammoniacal emulsion show that the desensitizing action depends on the length of the light exposure to which the photographic material is subject. The restoration of sensitivity on drying is more complete with the lower intensities and longer exposure times. The explanation given is that under the action of moisture there proceeds both an irreversible deactivation of sensitivity centers on which are formed small development centers and a reversible deactivation of centers which serve for the formation of large development centers.

The Problem of the Mechanism of Aging of Infrared Materials

A. S. KHEĬNMAN (Letter to the Editors), pp. 297–98

Experiments on the changes in sensitivity on aging of a high-speed negative emulsion sensitized with a tricarbocyanine dye are reported. The changes in sensitivity are explained as due to the formation of desensitizers, with an action similar to that of phenosafronin and pinakryptol yellow, formed by the oxidation of the sensitizing dye.

Scientific Discussion: Observations on the Article by A. L. Karpova on a Physico-Chemical Method of Analysis of Active Impurities in Gelatin

E. A. ZIMKIN, pp. 299–301

Further Considerations on the Nature of the Photographic Activity of Gelatin (with Reference to the Critical Observations of E. A. Zimkin).

A. L. KARPOVA AND K. V. CHIBISOV, pp. 301–08

Zimkin casts doubt on some of the earlier work of Karpova. He does not believe that thiosulfates are to be grouped with the "A-type complex formers" but believes that the thiosulfate in gelatins reacts with silver in the emulsions to form silver sulfide. He suggests that the second jump in Karpova's titration curves is not due to labile-sulfur containing compounds but to reducing agents. He also questions whether the first stage in Karpova's titrations is due to digestion retarders. In their reply, Karpova and Chibisov produce evidence in refutation of the first two points and give further experimental results on the nature and determination of the retarders, but agree that this last point needs further clarification.

The Physical and Photographic Fundamentals of Autoradiography as a Quantitative Method

A. L. KARTUZHANSKIĬ, pp. 309–16

The literature (twenty-five references) is reviewed.

The Photography of Luminescence of Capillary Fractions of Petroleum

L. I. OVCHINNIKOVA AND O. G. OZHGIKHINA, pp. 316–17, 1 pl.

A brief note is given on the camera and lighting set-up used in recording the luminescence of chromatograms of petroleum fractions on color film.

Something New in Cineradiography

L. YA. KAL', p. 318

Cineradiography of large areas of the body requires dangerously high x-ray dosage. The method suggested consists in taking a series of separate radiographs, such as is given by the apparatus used in angiography, and subsequently filming them with a cine camera. This method is convenient for cinematographically studying cyclic events of the body.

On Some Problems in the Coating of Photographic Emulsions on a Support

G. M. TSVETKOV, pp. 319–20

Some corrections are suggested in Deryagin and Levi's book *The Physical Chemistry of the Coating of Thin Layers on a Moving Base.*

Tekhnika Kino i Televideniya

Vol. 4, August 1960 (in Russian)

Résumés by S. C. Goddard

On the Possibility of Partially Replacing Gelatin in Photographic Emulsions by Synthetic Polymers

D. A. TSAREV, L. M. BOGDANOV, G. G. MARTYSH, AND V. I. LIPCHANSKAYA, pp. 8–11

Reported are the results of experiments in which up to 30% of gelatin in an emulsion was replaced by a synthetic polymer. The emulsion was one with a high silver-to-gelatin ratio and a large amount of residual soluble electrolytes. It was also used in its orthochromatically and panchromatically sensitized forms. The polymer (P-22) was a complex polyvinylacetal of o-sulfobenzaldehyde.

The polymer-containing emulsions were very stable to aggregation of the grains and hardened well with glyoxal. Coating, chilling, and drying of the emulsions proceeded normally, while the mechanical properties of the layers were considerably improved. The presence of the polymer had little effect on the photographic properties of the emulsion. The detailed results are tabulated.

The Measurement of the Light Scattering Coefficient of Cinematograph Objectives

F. S. NOVIK AND L. M. GLOTOVA, pp. 48–54

The research institute NIKFI has prepared an interdepartmental standard number MN 63-59 on the measurement of the light-scattering coefficient of cinematograph objectives, and apparatus has been constructed for carrying out the tests. This consists essentially of a photometric sphere with an aperture at one side from which light passes through the lens to be tested, while an aperture directly opposite serves as a dark object against a bright background. Light from the lens is received by a photoelectric cell connected to a galvanometer, the lens and cell being mounted on a rotatable arm so that the light passing through the lens can be measured at different angles. Measurements carried out on a number of lenses with this apparatus are tabulated and discussed. Generally speaking the Soviet-produced lenses show a somewhat higher scatter than imported objectives. Possible methods of reducing the scatter are discussed. It is suggested that limits should be set to the permissible light scatter of cinematograph objectives.

The Influence of an Underlayer and the Thickness of the Emulsion Layer on Halation and Resolving Power of Photographic Materials

I. A. NOVIKOV, pp. 69–70

A fine-grain positive emulsion and a coarser-grained negative emulsion were each coated directly on base and were also coated with an underlayer of the same, but undigested, emulsion. All specimens were tested for resolving power and halation. The results obtained are in conflict with general opinion. As the thickness of the emulsion layer was increased, resolving power fell and halation improved, while the presence of the underlayer caused a falling off in resolving power without any improvement in halation over that obtained with a directly coated emulsion of the same thickness. Possible explanations of these phenomena are discussed briefly.

Graininess and Granularity of Photographic Materials: II—Granularity of the Printed Image

S. OOUE (Research Lab., Fuji Photo Film Co., Miniami-Ashigara, Kanagawa Pref.), *J. Appl. Physics, Japan*, **29**: 528–35 (1960) (in Japanese, with abstract and figure legends in English)

This study was undertaken to determine the autocorrelation function of the grain pattern of the printed

image by using an optical autocorrelator, to obtain the power spectrum of the grain pattern by using the Fourier transformation, and to evaluate each spectrum so obtained. The autocorrelation function of the granularity pattern of the printed image consists of two components: One of these components, which has a shorter correlation distance, corresponds to the grain pattern of the positive film or of the x-ray film, and the other corresponds to the grain pattern of the negative film or of the fluorescent screen. The Fourier transform of the autocorrelation function was obtained and the contribution of each component to the magnitude of the graininess was determined. When Fuji motion-picture positive film was printed from Fuji Neopan SSS Film, the contribution of the grain pattern of the Neopan SSS Film was about one hundred times as large as that of the grain pattern of the positive film. When Fuji medical x-ray film was printed with a fluorescent screen, the contribution of the grain pattern of fine-grain fluorescent screens was about three times as large as that of the x-ray film, and the contribution of the grain pattern of coarse-grain screens was about ten times as large as that of the x-ray film. A quantitative comparison of the graininess of the two types of screens was made by this method. The response function of the printer optical system, which includes the spatial frequency characteristic of the positive materials and that of the printer, was obtained by using the power spectrum of the grain pattern of the negative film and that of the print. (Translation from author's abstract.)

• New Products and Developments

FRANK SMITH

• Cameras and Accessories

Vought Pulse Data Camera

Development of the VDR-4B 16mm Pulse Data Camera has been announced by the Vought Camera Co., 8907 Melrose Ave., Los Angeles 46, Calif. Specifications are as follows: 16mm pulse data recorder at frame rates up to 10/sec; cine operation at 16 frames/sec; accommodates any ASA "C" mount lens; power 28 v d-c; 100 ft daylight loading reels; size 4 by 5 by $7^5/_8$ in.; weight 8 lb. Shutter correlation and aperture two-light timing are available.

Two of the cameras were used on the record X-15 flights. Mounted within the fuselage and actuated by a cockpit switch, they photographed wing surfaces through a tiny porthole to record changes in stress and wing skin movement while the plane performed at high altitudes.

• Densitometers

Quantascan Automatic Recording and Analyzing Densitometer

Quantametric Devices, Inc., Binghamton, N.Y., has announced the Quantascan Model 101, which records the optical densities of photographic test strips, either paper or film, black-and-white or color. Features of the instrument are: (1) high operating speed (approximately 5 sec per strip), (2) automatic zero control, (3) conversion from reflection to transmission density with a single switch, (4) an electronic amplifier, linear with density, which utilizes modern solid-state components, and (5) ability to provide film speed, gradation, and other sensitometric data immediately upon completion of the recording cycle by means of analog computers attached to the recorder.

Optional features available include dual speed strip drive and dual density range (0-3 or 0-6).

Although the information contained in this section is compiled from sources believed to be reliable, the author cannot assume responsibility for its accuracy. Publication of the information here is not to be construed as an endorsement or recommendation of the product or equipment described.

• Illumination

Quantalumen Stable Calibrated Light Source

Quantametric Devices, Inc., Binghamton, N.Y., has announced the Quantalumen Model 141 power supply which maintains a selected 4-candle-power filament lamp at a constant intensity. The device is calibrated for candle power and color temperature and can be used with any 60 cps, 100–135-v source without meters, supplementary power supplies, or other auxiliary equipment. Candle-power ripple is estimated to be less than 0.0001%. The lamp assembly is nested within the stabilizer case for transport or storage. Warm-up time is 10 min at room temperature.

Characteristic tungsten radiation is emitted, and the instrument can be used for the absolute calibration or comparison of radiant energy detectors such as photoconductors, photoemissive cells, and barrier layer cells. When it is used in conjunction with calibrated filters or monochromators, the spectral sensitivity characteristics of receivers can be measured. Other uses include the calibration of optical and radiation pyrometers, and the secondary calibration of additional lamps for sensitometry.

Westgate Point Light Source Model PLS-6

Westgate Laboratory, Inc., Yellow Springs, Ohio, has announced development of a high-power point light source, for use where the light output from a grain-of-wheat lamp is inadequate or where the radiating tip must be unobstructed by a glass envelope. The light uses a 200-w Osram HBO 200 a-c-operated mercury-arc lamp and generates a light which is modulated at twice the line frequency (i.e., 120 cps). The arc size of this lamp is 2.5 mm by 1.3 mm. It features a tiny integral blower which keeps the lamp at the proper operating temperature. This model is furnished with a lucite tip if only low light output (25 to 50 lumens) is desired.

For higher light output (50 lumens or more), a quartz tip is required. The shape of the radiating tip is essentially a cone having a slightly rounded apex. The radiating portion of the tip has a base diameter of 0.75 mm and an altitude of 0.75 mm. The radius of the apex is $^1/_{64}$ in.

Special conical or rounded-apex conical tips of lucite or quartz are available in any dimension from 5 mm by 5 mm to 0.5 mm by 0.5 mm. The light output is directly related to the size of the radiating tip.

Duro-Test Corp.—Army Engineers Triple-Arc Xenon Lamp

A high-brightness high-pressure xenon-arc lamp for long-range illumination has been developed by the Duro-Test Corp., North Bergen, N.J., in cooperation with the U.S. Army Engineer Research and Development Laboratories, Fort Belvoir, Va.

Xenon high-pressure high-brightness bulbs are a new type of powerful lamp for military use, searchlights, projectors, and space applications. The rays of the Xenon lamp can be projected for a distance of 50 miles. In one envelope, the lamp has three brilliant arc discharges spaced approximately $^1/_4$ in. from one another, which can be switched and regulated independently, making the lamp particularly useful for military and space applications.

Advantages of xenon-arc over carbon-arc lamps are clean maintenance-free operation, absence of an open flame, freedom from fumes, daylight color of light, and long life of up to one thousand hours.

G-E Flexible Electroluminescent Light Sources

Development of electroluminescent light sources five times brighter than any other now commercially available has been announced by the Miniature Lamp Department, General Electric Co., Nela Park, Cleveland, Ohio. The sources, which are in the form of flexible plastic panels about the thickness of a magazine cover, will be available in green, blue, yellow, and white, and in sizes ranging from 1 by 1 in. to $11^3/_4$ by 14 in.

Initial brightness in foot-lamberts, operating on 60-cycle, 120 v ac, is 4.5 for green, 1.5 for yellow and white, and 1.0 for blue.

• Optics

Miniature Lens with Hemispheric Coverage for 35mm Cameras

The Traid 735 Wide-Angle Lens, designed and manufactured tc Traid Corporation specifications by the Pacific Optical Company, has a 180° field of view, a focal length of 6.51 mm, and aperture of $f/6.3$; it is in a rugged Eyemo mount. This miniaturized lens is primarily for use in drone scoring systems, but can be used in other situations requiring extremely wide-angle coverage.

Zoomar Collimator

Zoomar Inc., Glen Cove, N.Y., has developed a portable field collimator which checks long focal length lenses in the field. The Zoomar Service Collimator is based on the premise that a collimator objective need not have a focal length longer than the lenses tested if it is corrected over a considerable extra-paraxial field. It is also considered unnecessary to cover the entire area of the lens under test. For measurements of the focal plane position and chromatic aberrations, it may be advantageous to examine portions of the lens successively when checking for symmetry and possible cylindrical conditions.

Based on these concepts, Zoomar, Inc., designed a lightweight, portable collimator of convenient dimensions which will serve particularly well the needs of the Armed Forces.

Features of the collimator include a "Thermar" mounted apochromatic catadioptric system of 150 in. E.F., standard U.S. Air Force target (other targets optional), 300 lines/mm resolution, with micro-adjustable legs for easy set-up. It is suitable for selective part coverage for testing lenses of very large diameters. The collimator measures 10 by $6^1/_2$ by 30 in., and weighs 25 lb.

• Rapid Processing Equipment

Application of Liquid to Surfaces

U.S. Patent No. 2,956,494 (Oct. 18, 1960, Frank Tyler, et al., Assignors to Kelvin and Hughes, Ltd., Glasgow, Scotland), is for an improved apparatus for continuous rapid processing of photographic film. It consists of a processing head having a narrow cup or recess provided with an inlet and an outlet opening for the processing fluid, and a means for maintaining the film to be processed spaced a short distance from the edges of the cup or recess. A reservoir is provided for the processing fluid and a means is provided for applying suction to the cup or recess, the arrangement being such that processing fluid in the reservoir can be delivered to the cup or recess while air is drawn into the cup or recess through the space between the cup or recess and the film.

The essential difference between this invention and others of the cup or recess type is that the film being processed is maintained a short distance from the edges of the cup, thereby preventing damage to the film as it is moved past the cup. This distance is such that the film makes contact with the meniscus of the processing liquid in the cup. The inventors claim that the effect of drawing air into the gap between the cup and the film is to create an air cushion which constitutes an effective extension of the side walls of the cup.

If required, separate processing heads placed in sequence along the moving film to be processed may be provided and so arranged that each station uses and circulates one fluid only.

System for Rapid Processing of Photographic Film

U.S. Patent No. 2,922,353 (Jan. 26, 1960, E. F. Berley, Assigned to General Aniline and Film Corp., New York, N.Y.), is for a design for spraying film with a plurality of processing solutions in sequence through a single nozzle. The nozzle is connected to a supply tube, which in some instances may be a capillary type, and means are provided for charging the tube with separate quantities of distinct processing solutions and interposing gas bubbles between each of the solutions. Pressure means are included for expelling the contents of the tube in sequential order through the nozzle.

In addition, an air nozzle is positioned adjacent to the solution nozzle for introducing a gas for drying the film and to supply additional kinetic energy to the jet of solution emerging from the solution nozzle. This arrangement provides a controlled droplet size.

The inventor states that the processing system is inherently self-cleaning after each cycle of operation.

• Reproduction and Copying

APECO "Electro-Stat" Electronic Copymaker

An office copying machine, based on the Electrofax Process of the Radio Corp. of America, has been an-

nounced by American Photocopy Equipment Co., Evanston, Ill. The unit produces black-and-white copies of any business paper, even those containing halftones, solids, and colored material, at the rate of 5 copies per minute. The process requires no liquids for operation. The copier is 18 by 24 by 24 in. and weighs 100 lb. It operates on 115 v ac.

Army Engineers Electrostatic Color-Map Printing

A printing machine designed to reproduce colored maps by means of an electrostatic process is under development by the U.S. Army Engineer, Geodesy, Intelligence and Mapping Research and Development Agency, Fort Belvoir, Va. The printing method is based on the phenomenon of the mutual attraction between particles having opposite electrical charges. The process uses a photoconductive coating applied to paper.

The experimental single-color machine being tested was built by the Radio Corp. of America and reproduces maps directly from miniature separation transparencies. The elimination of platemaking requirements makes map reproduction possible in much less time than by the present lithographic process.

Studies and tests of the experimental model are expected to lead to the development of a five-color electrostatic printing machine capable of reproducing 2000 multicolor maps per hour.

• Miscellaneous

Multiple Sound Tracks

U.S. Patent No. 2,950,971 (Aug. 30, 1960, George Lewin, Brooklyn, N.Y.), relates to an improvement in the combination of optical and magnetic sound tracks arranged to occupy the same space. The full width of the allotted space may be occupied by each of the sound tracks, and the presence of the magnetic sound track will not cause the introduction of noise and distortion during the reproduction of the optical sound-track recording. This arrangement permits the optical sound track to be recorded in the usual manner, while a magnetic sound track is simultaneously recorded on the same film. Both sound tracks are reproducible simultaneously or separately, after development of the film.

The magnetic stripe is laid over the photographic emulsion, thus protecting the optical sound track from wear. Reproduction of the optical sound track is effected by projecting an infrared beam through the magnetic stripe to an infrared-sensitive photocell, the magnetic stripe being transparent to infrared.

SORTI Missile Tracking System

A study contract to develop the design for a "real-time" highly accurate missile tracking system has been awarded to Radiation, Inc., Melbourne, Fla., by the Air Force Missile Test Center. To be known as SORTI (Star-Oriented Real-Time Tracking Instrument), the tracker will combine the high accuracy of the ballistic camera system, with a real-time position tracking system.

In the focal plane of a ballistic camera lens is a narrow slit with a photomultiplier detector tube behind it. A rotating mirror effects alternate scans of the sky in x- and y-directions. A clock tied to the mirror rotation counts increments of angular measurement, and its output is gated by the detector tube so as to provide an accurate reading of the angular displacement between two celestial light sources such as a missile and a known star. An IBM 7090 computer is available to calculate quickly the true angular position of the star at any instant of time. The method permits accurate missile location with a minimization of errors caused by atmospheric refraction, instrument misalignment, etc. The accuracy desired is 1 sec of arc at a 20/sec repetition rate.

Stromberg-Carlson High-Speed Communications Printer

Stromberg-Carlson Division of General Dynamics Corp., San Diego, Calif., has developed the S-C 3000 High-Speed Communications Printer. The printer utilizes a compact version of the Charactron Shaped Beam Tube for presentation of information, which is then recorded on paper by means of an electrostatic process at speeds up to 10,000 characters per minute.

Hydel 35mm Film Reader

The Model 200 35mm Film Reader for accurately measuring the positions of points on film, has been announced by Hydel Inc., 223 Crescent St., Waltham 54, Mass. The reader is for use in connection with bubble chambers, cloud chambers, meteorology, and target or missile tracking. Provision is made for scanning or reading any one of three motor-driven films. Resolution and repeatability is 1 μ and full-scale accuracy is better than ± 5 μ through a 50 by 50-mm. range. Information is automatically fed to data storage.

The operator sits before a daylight screen where the image of the 35mm frame under inspection is projected at 20× magnification. Superimposed on the screen, and also magnified, is a movable reticle for measuring purposes.

Ansco Microdensitometer

Ansco, Binghamton, N.Y., has announced the Automatic Recording Microdensitometer, Model 4, which is designed for accurately measuring and recording transmission and reflection densities of micro images. Although originally designed for specialized photographic application, the instrument is now being used in fields where accurate measurement of optical image characteristics is required.

Recordak Microfilm Reader

The Recordak Model 310 Microfilm Reader, which weighs 23 lb and is less than 20 in. high, has been announced by Recordak Corp., 415 Madison Ave., New York 17, N.Y.

Features of the reader, which will accommodate 16mm unperforated microfilm in 100-ft lengths, include full 90° image rotation on a 9 by 12-in. viewing screen and a film advance handle on the side of the machine. Reduction ratios available are 20:1, 24:1, 32:1, or 40:1. A basically similar reader, the Model 310-A, featuring 270° image rotation, was designed for installations where the duo method of microfilming is in use.

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• Advance Program—1961 Annual Conference

Society of Photographic Scientists and Engineers

Members of the SPSE and nonmembers are invited to participate in the 1961 Annual Conference, which will be held May 22–26 at the Arlington Hotel, Binghamton, New York. Every effort has been made to prepare a program balancing the scientific and the engineering aspects of the photographic field. At this time, the program is as complete as possible, but experience has shown that minor departures are unavoidable.

Monday, May 22

Circuit for Adjusting Automatic Color Printer Response, *R. K. RICKARD, Eastman Kodak Co., Rochester, N.Y.*

Several factors can cause changes in over-all density and color balance when color prints are made by additive printing methods from color negatives that vary in average density. A simple electrical circuit has been designed to compensate automatically for most of the effects of these factors. The circuit is arranged to vary the log of print exposure linearly with negative density. The amount of change in exposure can be adjusted for each color to vary the slope of the printer response curves.

Filtration and Monitoring Systems for Color Printing, *R. B. CALKIN and R. W. HUNT, Kodak Ltd., Harrow, England, and E. K. LETZER, Eastman Kodak Co., Rochester, N.Y.*

Three independent variables must be controlled in the successful printing of color negatives. While independent red, green, and blue exposures can be controlled as the three variables, a more efficient method is provided by a filtered white-light printing system. A variety of filtration systems will be described with particular emphasis on several methods employing sliding filters. The most sophisticated of these arrangements requires specially manufactured filters but provides the simplest and most straightforward operation.

Investigation of Additive Color Photography and Projection for Military Photo-Interpretation, *RICHARD P. WINTERBERG and JOSEPH W. WULFICK, Dunlap and Associates, Santa Monica, Calif.*

A number of research hypotheses concerning the application of an additive color photography system for military photo-reconnaissance are presented. Based on military requirements and properties of additive color photography, certain predictions are made as to the potential of such a system for increasing the photo-interpretation capability. Initial laboratory experimentation is under way to evaluate the predicted capabilities of additive color techniques. Results to date will be reported and demonstration slides will be shown.

Color Photography as an Aid to Photo-Interpretation, *JOHN WALKER, Broadview Research Corp., Washington, D.C.*

Present aerial color photography has definite advantages over black-and-white for interpretation of specific detail. Modifications of present techniques to improve color photography for interpretation purposes are discussed, including recent research on the spectral reflectance of ground objects which appear as images in aerial photography. Illustrations of camouflage detection photographs, conventional aerial photographs exposed with various filters, and curves of reflectance data obtained from soils and vegetation will be shown. General features required of an aerial film for highly accurate extraction of detailed information are outlined.

Granularity Measurement of Color Film, *SHINGO OOUE, Fuji Photo Film Co., Ltd., Minamiashigara, Kanagawa, Japan*

In addition to light-intensity variations commonly associated with granularity of black-and-white films, color films require a consideration of the chromaticity variations as well. The analysis of such variation is discussed, and evaluation techniques and practical results are presented.

Optimization of the Characteristic Curves for Reversal Film, *G. W. SCHUMANN, Ansco, Binghamton, N.Y.*

The tone-reproduction curves for preferred black-and-white reflection prints are S-shaped, having a ratio of approximately 0.70 between their average and maximum gradients. Under the assumption that this is valid for transparencies also, it is possible to calculate hypothetical characteristic curves. A figure of merit calculated from the reproduction scales and exposure latitude serves to select the optimum curve from an infinite number of possible solutions.

The Standardization of Correct Exposure of Reversal Film under the Aspect of Probability Theory, *W. BEHRENDT, Agfa, Leverkusen, Germany*

The sum of maximum errors in the various factors influencing the exposure is of the order of ±3 stops. This value corresponds to practical experience in film processing labs and exceeds the film tolerances. Conditions with automatic cameras are more severe and narrow tolerances in all stages are required. Reduction of camera and projector flare would make it possible to design films with lower gradients and higher exposure latitude.

The Optimal Gradation and the Optimal Exposure of Color Reversal Film, *W. BEHRENDT, Agfa, Leverkusen, Germany*

The optimum tone-reproduction curve for reversal film is a straight line with a gradient of 1.00. The theoretical sensitometric curve is calculated for a flare of 2%. In this case the optimum gradient in the straight-line portion is in the order of 1.80, and the curve has a pronounced toe.

On the Preferred Reproduction of Flesh, Blue Sky, and Green Grass Colors, *C. J. BARTLESON and C. P. BRAY, Eastman Kodak Co., Rochester, N.Y.*

The preferred reproduction color for complexions in color prints and projected color transparencies has the same chro-

maticness as the mean memory color for flesh. This color is perceptually and statistically significantly different from the chromaticity of the average for natural Caucasian flesh colors. However, the preferred reproduction chromaticities for blue sky and green grass appear to be of the same hues as those implied by the chromaticities of the average natural objects. It will be shown that the desirable objective of a color reproduction system is neither faithful reproduction of the original chromaticities nor of those corresponding to the mean memory colors. Experiments will also be described in which the general ability to remember colors was tested by successive color matching.

Psychophysical Methods for Evaluating the Quality of Color Transparencies, *C. J. BARTLESON and W. W. WOODBURY, Eastman Kodak Co., Rochester, N.Y.*

A series of experiments have been carried out to devise an efficient and precise method of evaluating the quality of projected color transparencies. It was determined that categorical and comparative judgment methods yield the same results when properly controlled. The categorical judgment method is less tedious and less time-consuming, but it is necessary to control or stabilize the observer's frames of reference to a constant, standard and known level. The factors that influence the judgment data will be discussed and a method of control described that appears desirable for obtaining precision and invariance of the controlled reference level.

Tuesday, May 23

Camera Calibrator, Model III, *GOMER T. McNEIL, Photogrammetry, Inc., Silver Spring, Md.*

The Camera Calibrator, Model III, is a precision instrument designed to provide a symmetrical array of targets. This array is photographed by the camera to be calibrated. The images of the targets are then measured on the negative to yield the necessary data for the determination of focal length, location of principal point, radial and tangential distortion, and radial and tangential resolution.

On the Spatial Stability of Photographic Plates, *J. H. ALTMAN and R. C. BALL, Eastman Kodak Co., Rochester, N.Y.*

The shifts in the positions of images recorded on photographic plates that occur during processing and drying of the emulsion layer have been investigated. Position data for 48 points in a two-dimensional master grid and of their images were obtained and compared by means of an electronic computer. The root-mean-square value of position error was computed for various types of fit. The findings of this investigation will be described, and the effects of a few variations in exposure and processing on random spatial errors will be discussed.

Test Methods for Rating the Abrasion Resistance of Photographic Film, *J. F. CARROLL and J. O. PAUL, Eastman Kodak Co., Rochester, N.Y.*

Different methods of rating the abrasion resistance of photographic film are compared. The spherical stylus method was found to be most versatile. The results on six different films under various conditions of surface friction, lubrication, and relative humidity indicate that the method which most closely approaches the suspected abrasion mechanism should be considered most valid.

Image Sharpness Meter, *DWIN R. CRAIG, Log-Etronics, Inc. Alexandria, Va.*

The meter reading of a photoelectric device is a quantitative indication of the sharpness of an image projected onto the surface of its sensing element. The recognition of image sharpness depends on the mathematical fact that the Log (A+B) is not equal to Log A plus Log B. With the sensing element on the easel of an enlarger, the meter reads full scale when a halftone screen in the negative carrier is sharply focused on the easel and drops to zero when the image is not in focus. Finger pressure on the lens board will cause the meter to fall to half scale. Possible applications of the device include a focus indicator, auto-focus control, lens testing equipment, image coincidence detector, microcontrast meter, and others.

A New Method and Apparatus for Evaluating the Susceptibility of Photographic Materials to the Accumulation of Electrostatic Charges, *R. A. FRIEND and PETER KRAUSE, Ansco, Binghamton, N.Y.*

An apparatus has been constructed with which electrostatic charges may be applied to a test sample by means of a corona charging unit. The rate of decay of the charge can then be measured and the event displayed graphically on an oscilloscope screen where it may be viewed and photographed. The construction and mode of operation of the apparatus will be described and test data discussed. The use of xerographic powder development techniques for the detection of electrostatic charge patterns on photographic film surfaces will also be described.

A Photoelectric Lens Bench for Rapid Routine Testing of Interchangeable Lenses, *WILLIAM T. SHERWOOD, Eastman Kodak Co., Rochester, N.Y.*

A vertical lens bench was designed for the testing of 35mm camera lenses, employing a tungsten light source, a Nipkow scanning disk, and a photomultiplier tube. The light passes twice through the lens, and the results are displayed on a cathode-ray tube.

Wednesday, May 24

An Advanced Photographic Subsystem Design (KS 25 Camera), *GEORGE E. DENNEWITZ, Wright-Patterson Air Force Base, Ohio*

A high-acuity aerial camera with a newly designed stabilized mount and associated controls constitute the airborne part of a research subsystem to study photographic reconnaissance. The quality of the image collected is preserved by a ground handling subsystem including a standard USAF processor, a new resolution sensitometer, a precision high-acuity printer, and a stereo-viewer.

Panoramic Cameras for Aerial Surveillance, *KARL G. LEISTNER and DIETER P. PARIS, U.S. Army Signal Research and Development Laboratory, Fort Monmouth, N.J.*

In recent years, there has been a revival and refinement of a camera design which had a moderately wide distribution in the early twenties and then disappeared almost completely: the panoramic camera. Its present application for scanning the essentially horizontal surface of the earth from a fast-moving airborne platform creates a number of problems not apparent in the old design. Primarily, these are: the continuously changing object-to-image scale and other deformations of the image; limitations on resolution; image-motion compensation; means of rectifying the image; and suitable viewers for panoramic pictures. These problems as well as different methods used or proposed for their solution will be discussed and analyzed.

A High Resolution Exposure Determinant for Aerial Films, *MARILYN LEVY, U.S. Army Signal Research and Development Laboratory, Fort Monmouth, N.J.*

A simplified system is described, whereby the exposure yielding maximum detail can be determined from any sensitometric H&D curve. This system was developed after analyzing the resolution-vs.-exposure curves of representative aerial films at varying development times. The exposure required for maximum resolution for these films was found to be equivalent

to the exposure required to yield a density of 0.85 above fog. Actual camera exposures, based on this 0.85 exposure criterion were determined and applied successfully on aerial photographic missions. This exposure determinant system can also be modified to obtain the exposure required for 0.9 maximum resolution. The use of the 0.6-gamma speed criterion is also discussed.

Reproduction of High-Acuity Aerial Photography, *A. W. BERG, Wright-Patterson Air Force Base, Ohio*

Optimum reproduction procedures are presented for preserving the maximum amount of information from very high-quality aerial negatives. Each element of the photographic reproduction process is analyzed for minimization of resolution loss. New methods of measuring and evaluating the performance of such processes are given, and the relationship of these measurements to actual performance is discussed.

Viscous Techniques for Airborne Processing, *EDWIN BELLMAN and LEO LANG, Fairchild Camera and Instrument Co., Syosset, L.I., N.Y.*

Basic methods for utilizing viscous solutions in airborne processing are described, including monobath and two-stage techniques. Chemistry, sensitometry, and design features are discussed, along with the analysis and solution of a typical problem.

A Photopolymerization Method for Preparing Three-Dimensional Terrain Models, *C. J. CLAUS, I. T. KROHN, and P. C. SWANTON, Haloid Xerox, Inc., Rochester, N.Y.*

A photomechanical method based on dye-sensitized photopolymerization, is described for the preparation of three-dimensional terrain models. The procedure involves polymerization of an aqueous monomer solution by visible light. A contour map transparency, in which increasing height is represented by decreasing density, is projected into the photosensitive solution. Since the monomer is polymerized by visible light, a three-dimensional terrain model results.

Designing Semiconductor Programmers for Photography, *D. A. CHUBB, Abrams Instrument Corp., Lansing, Mich.*

Photographic programmers are simple computers which now have many functions involving synchronization, lighting, delay, computation, error detection, etc. To illustrate the use of semiconductors in a photographic programmer, the design of the Abrams Instrument Corporation AP-1 (airborne programmer) will be reviewed. This review will include protective features insuring performance under various environmental conditions and basic circuit-design features.

Photographic Plates as Computer Memory Devices for Radar Simulators, *R. J. ENTWISTLE, U.S. Naval Training Device Center, Port Washington N.Y.*

A new class of radar simulators uses a pair of precisely oriented images on a transparent photographic plate as the information input for the system. Data stored on the plates are read out with a flying spot scanner and operated on by a computer to complete the simulation.

Determination of Minimum Element Size in Factored Transparency Radar Simulators, *LEO LEVI, Consultant, New York, N.Y.*

In the "factored transparency" technique, various terrain characteristics are represented in the form of densities on photographic film. The turbidity and granularity characteristics of the photographic emulsion limit the accuracy with which the density of an area element in a photographic transparency may be controlled. The basic relationships between element area and obtainable accuracy are given in terms of the emulsion point-spread function, its Selwyn granularity, the density distribution on the transparency, and the light distribution in the scanning spot. As an example, these relationships are applied to a transparency representing altitude.

The Quantascan Ω—A Universal Photometer, *M. H. SWEET, Quantametric Devices, Inc., Binghamton, N.Y.*

A new general-purpose photometer is described, consisting of a portable probe unit containing the photomultiplier tube and filters and an amplifier readout unit. The amplifier incorporates both a logarithmic and a linear mode. A small stabilized reference lamp and neutral density filter wheel are included in the amplifier chassis to permit instant checking of the probe unit. An automatic zero adjustment is incorporated for use in the logarithmic mode.

A High-Speed Electromechanical Shutter, *PAUL A. KENDALL, U.S. Naval Ordnance Laboratory, Silver Spring, Md.*

An electromechanical shutter with submillisecond open time was designed and constructed for accurately controlling the recording period of a Bausch & Lomb medium quartz spectrograph. By mechanically harnessing the magnetic field set up by a high current surge through a small flattened wire, a slotted shutter located in front of the slit of a spectrograph is opened in about 15 μ sec after the shutter is triggered. The open time of the present shutter can be varied from 100 to 500 μ sec and its closing time is about 5 μ sec. The shutter plate can be easily modified so that the minimum open time and closing time are each about 1 μ sec.

A High-Speed Automatic Film Cutter, *WILLIAM C. KLEIN, Eastman Kodak Co., Rochester, N.Y.*

A high-speed (linear film speed, 24 in./sec) photographic film cutter can accommodate all standard film widths from 35mm to $3^1/_2$ in. The film may be cut into individual frames or into short strips of 2, 3, or 4 frames, depending on the setting of a selector switch. The cutting mechanism is activated by means of a small perforation put into the film during the printing operation. Fail-safe and other protective circuits are used extensively to protect the negatives from spurious cuts.

A Review of the Wet Plate Process, *I. B. CURRENT, Ansco, Binghamton, N.Y.*

On the occasion of the Civil War Centennial, the wet plate process as practiced by Brady was reviewed. Sensitometric parameters of the process have been studied, using present-day techniques. In view of the variations possible in coating, sensitizing, and development, we are forced to admire the photographic quality Brady and his contemporaries achieved with a material that would have had an ASA speed of about 0.05. Wet plate photographs were made with an old-style camera and old-style equipment in the course of this undertaking, and examples of these photographs will be shown.

Thursday, May 25

The Effect of Negative Granularity on the Tone Reproduction Characteristics of the Print, *L. D. CLARK and C. N. NELSON, Eastman Kodak Co., Rochester, N.Y.*

When the grain pattern of a negative is reproduced in a print, it will behave like a halftone dot pattern to an extent determined by how sharply the grain pattern is reproduced. This factor influences the shape of the tone reproduction curve, particularly in the highlight region if the negative grain pattern is sharply reproduced in the print. A new projection printing technique was applied for obtaining grainless and grainy enlargements from the same negative.

The Halftone Effect in High-Resolution Printing, *J. H. ALTMAN and R. M. PEDEN, Eastman Kodak Co., Rochester, N.Y.*

The halftone effect described by Clark and Nelson may be encountered in a special form when grainy negative materials are contact printed, if the resolution of the printer and print stock are high enough to image the individual grains of the negative material sharply. The nature of the halftone effect and the occurrence of random density blotches in high-resolution contact printing has been investigated by means of a simple device. Quantitative data will be given relating the magnitude of the density differences to the graininess of the negative and the spread functions of printer and printer stock.

Influence of Image Motion on the Resolution of a Photographic System, *DIETER P. PARIS, U.S. Army Signal Research and Development Laboratory, Fort Monmouth, N.J.*

The influence of three types of image motion—linear, vibration, and random—on the photographic reconnaissance system is discussed. Curves are presented showing the decrease in photographic resolution for known motions of the image plane. An attempt is made to interpret these curves by the concept of sine-wave response.

An Objective Method for Predicting Picture Sharpness, *EDWARD M. CRANE, Eastman Kodak Co., Rochester, N.Y.*

Sine-wave response has been treated as a fairly abstruse concept in physical and psychophysical optics. The frequency response of a complex system (object-camera-film) is applied to predicting image sharpness in commercial color films, and an empirical sharpness rating is proposed.

The Contrast Transmission of a Sinusoidal Signal of Large Amplitude by Photographic Materials, *HENRI THIRY, University of Liège, Belgium*

Lloyd's mirror interference patterns are used to determine the transmitted contrast of sine waves on photographic film. The limiting resolving power is measured at that point where the contrast (ordinate)-vs.-frequency curve levels out horizontally due to granularity. The total curve describes the resolving power characteristics of the film material.

Photographic Film as an Element of a Coherent Optical System, *EMMETT N. LEITH, University of Michigan, Ann Arbor, Mich.*

In coherent optical systems, the film transfer functions, the dynamic film range, and the film noise spectrum were measured for a number of films. A relief image obtained in developed photographic pictures influences coherent systems and may be either utilized or excluded by a liquid gate.

Film Response as a Function of Exposure, *F. SCOTT and M. D. ROSENAU, JR., Perkin-Elmer Corp., Norwalk, Conn.*

Square-wave or sine-wave targets of a given contrast and of several spatial frequencies are photographed with a high-resolution camera. The modulation of the processed images is then measured with a microphotometer. The measured modulations together with granularity data are plotted as functions of exposure to determine optimum exposure, loss of image quality at nonoptimum exposure level, and requirements for exposure control mechanisms. The response of film is determined by comparing the modulations in the photographic and the optical images. Application of this technique to evaluation of aerial film will be discussed.

A Technique for Analyzing Photographic Transparencies, *R. M. SCOTT, R. V. SHACK, and F. SCOTT, Perkin-Elmer Corp., Norwalk, Conn.*

The image structure of monochrome photographic transparencies is analyzed by an instrument which in basic principle is a grating spectrometer. The scene itself is analyzed, so that special evaluation targets are not needed. The results obtained are a function of the spatial frequency of the image structure, the distribution or volume of the scene, and the geometry of the scene. The detection and measurement of factors contributing to image quality by this technique are discussed.

PANEL DISCUSSION

Communication Theory in Photography, *Chairman, R. CLARK JONES, Polaroid Corp., Cambridge, Mass.*

The Enhancement of Print-out Effect by Bathing Treatment, *Y. TOMODA, Government Chemical Industrial Research Institute, Tokyo, Japan*

The print-out effect of a motion-picture positive emulsion was enhanced by bathing with certain metal salts, organic reducing agents, organic acids, and sulfur and nitrogen compounds. The mechanism of this sensitization and possible applications, such as radiation dosimetry, will be discussed.

Friday, May 26

Photopolymerization Induced by Metal Salts: Part I—Silver Salt Catalysts, *STEVEN LEVINOS and F. W. H. MUELLER, Ansco, Binghamton, N.Y.*

Investigations have demonstrated that soluble and insoluble silver salts when embedded in a gelatin layer containing a vinyl monomer can be photoactivated by ultraviolet radiation and, if optically sensitized, by radiation in the visible wavelength spectrum to induce polymerization. This polymerization takes place in a dry gelatin layer concurrent with the exposure. Subsequent washing of the layer yields relief images. Possible mechanisms by which this reaction occurs are proposed.

Photopolymerization Induced by Metal Salts: Part II—The Iron Salt-Peroxide System, *F. W. H. MUELLER, H. EVANS, and E. CERWONKA, Ansco, Binghamton, N.Y.*

It was observed that light-sensitized trivalent iron salts, imbedded in a gelatin coating, can be photoreduced to bivalent iron salts which can serve as catalysts for imagewise vinyl-polymerization if a suitable monomer and a peroxide are also contained in the layer. An alternate method for achieving this polymerization is to omit the peroxide from the layer and bathe the exposed layer in a solution of hydrogen peroxide. The polymerization takes place in the dry coating upon exposure with ultraviolet and visible radiation. Subsequent washing yields relief images. A possible mechanism will be proposed.

Photopolymerization Composition Containing Aromatic Diazo Compounds, *A. K. SCHWERIN and F. W. MILLARD, Ansco, Binghamton, N.Y.*

Polymeric photographic images can be obtained by utilizing the inhibiting effect of the photodecomposition products of aromatic diazo compounds. It was found that such decomposition products, presumably of a phenolic nature, are capable of inhibiting the ferrous ion-peroxide-initiated polymerization of a vinyl monomer. These findings have been applied to a direct positive image recording system.

The Temperature Dependence of Spectral Sensitization by Dye Series of Regularly Increasing Chain Length, *W. WEST, Eastman Kodak Co., Rochester, N.Y.*

The efficiency of spectral sensitization at exposure temperatures from 25°C to −196°C was examined for sensitizing dyes of the 3,3′-diethylthiacyanine series from the dye of shortest chain length to the tricarbocyanine, and for a similar vinylogous series of merocyanines, in chlorobromide and bromoiodide emulsions. No systematic variation of the

temperature coefficient of sensitization with wavelength appeared, either with respect to the absorption bands of the different members of a vinylogous series, or at different wavelengths in the absorption band of a given dye or a given emulsion. Certain conclusions about the process of spectral sensitization are drawn from these results.

Effect of Temperature of Exposure of Photographic Sensitivity and the Rate of Development, *T. H. JAMES, W. VANSELOW, and R. F. QUIRK, Eastman Kodak Co., Rochester, N.Y.*

Latent image formed at −196°C develops much more slowly than that formed at room temperature; hence the relative photographic sensitivities depend on the duration of development. The development rate for latent image formed at low temperature is greatly increased by gold latensification. Some conclusions on the mechanism of latent-image formation and the role of interstitial silver ions are drawn.

Photographic Developing Agents: 3. Heterocyclics, Dyes, and Aromatic Compounds of Unusual Structure, *RICHARD W. HENN and PRISCILLA S. COSTICH, Eastman Kodak Co., Rochester, N.Y.*

Developing activity is described for a number of compounds of unusual structure. While some of these are reduced to active developing form by the sulfite present in the developer solution, and the relation of others to known agents is obtained by analogy, the activity of a number of compounds does not fit any of the usual rules. The structural conditions essential to the developing properties are delineated by the testing of analogous compounds.

Interaction of Silver Sulfide and Bromine during Latent-Image Formation, *D. A. NEPELA, Ansco, Binghamton, N.Y.*

Evidence for the interaction of bromine with the silver sulfide sensitivity centers of normal photographic emulsions is presented. This evidence is based largely upon the behavior of a novel reversal system utilizing this interaction to effect reversal without the usually required second exposure or second development. The effect of pH, pBr, sensitizing and desensitizing dyes upon the system is considered. The reversal effect is discussed in the light of current concepts of the role of sulfur sensitization in latent-image formation. Electron-microscope studies support the conclusions reached.

Superadditivity in Photographic Development Studies of a Series of Substituted Hydroquinones with 1-Phenyl-3-Pyrazolidone, *W. E. LEE and T. H. JAMES, Eastman Kodak Co., Rochester, N.Y.*

The rates of photographic development by solutions of 1-phenyl-3-pyrazolidone ("Phenidone") and various hydroquinone derivatives have been investigated to test the effect of substituents on the degree of superadditivity. Developments of an exposed conventional photographic emulsion were carried out as well as solution-physical developments of an unexposed emulsion coated with Carey-Lea colloidal silver. The Phenidone-hydroquinone combination was found to be superadditive for both types of development in a pH range of 8 to 10. A reaction scheme is proposed which is compatible with the experimental observations and which accounts for the increased activity of Phenidone in the presence of hydroquinone.

The Characteristics of Physical Development with Developer Solutions Containing Thiosulfate-Silver Complex Ions, *R. M. COLE and R. B. PONTIUS, Eastman Kodak Co., Rochester, N.Y.*

Effectively stable physical developers containing silver ion supplied by dissociation of a thiosulfate-silver complex have been used to study the kinetics of pure physical development onto colloidal silver nuclei dispersed in a plain gelatin coating. A comparison of physical development rates of two *p*-phenylenediamine type of developers with *p*-phenylenediamine itself and a metol-hydroquinone developer has been made. The effects of pH, silver-ion concentration, developer concentration, and the effect of buffer ion on the rate of physical development have been measured.

The Electrolytic Removal of Thiosulfate from Processed Photographic Papers, *R. E. RICE, Ansco, Binghamton, N.Y.*

A method for the electrolytic removal of thiosulfate and silver thiosulfate from processed photographic papers will be discussed, along with a description of a device to accomplish the removal. The method is based on the ion mobility of thiosulfate and silver thiosulfate in an electrolytic field. A breadboard model of a washing device was designed to accomplish washing to archival quality in a total time of 5 min vs. 30 min or longer by conventional washing methods.

Adsorption of Development Restrainers to Silver and Their Effects on Physical Development, *ROBERT J. NEWMILLER and R. B. PONTIUS, Eastman Kodak Co., Rochester, N.Y.*

The adsorption of 1-phenyl-5-mercaptotetrazole, benzotriazole, and potassium iodide on a metallic silver surface was determined. The results were subsequently utilized in physical development studies on colloidal silver coated in gelatin. Inhibition of development occurs when a restrainer adsorbs to the surface of the silver and forms a nonconducting layer which prevents the electron transfer from the developer to the silver ion.

This Advance Program has been prepared by the Papers Committee.

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